

CRYSTALLINE FORM
AND
CHEMICAL CONSTITUTION



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Crystalline Form and Chemical Constitution

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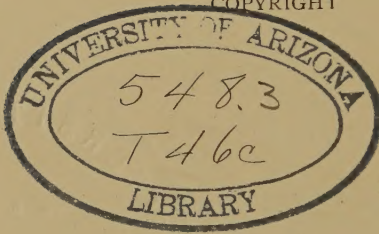
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THE AUTHOR TO HIS COUSINS
SIR JOHN CECIL POWER, BART., M.P.

AND

LADY POWER

WHO HAVE SO GENEROUSLY PROVIDED HIS EXCELLENT
NEW LABORATORY IN CAMBRIDGE,
AND HAVE EVER TAKEN SUCH DEEP AND
ENCOURAGING INTEREST
IN HIS CRYSTALLOGRAPHIC RESEARCHES

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PREFACE

THIS account of the present position of Chemical Crystallography, a subject now become of prime importance on account of its vast recent developments, is based on a course of lectures delivered in the Easter Term of 1925 at Cambridge University. An attempt is made, however, to render it more generally suitable, not only for students of Chemistry, Physics, Physical Chemistry, and Mineralogy, but for a wider circle of readers, by the inclusion of a preliminary chapter (Chap. I) in which the essential facts of pure Crystallography are very concisely summarised, in order that those readers who have not hitherto studied the subject may be provided with the minimum knowledge regarding the nature of crystals and crystal structure, including the latest development of the analysis of crystals by X-rays, which is necessary for a proper comprehension of the relations between crystal form and chemical constitution. This chapter may, therefore, be passed over by readers who have taken an adequate course of pure Crystallography, but even these may find it convenient to have the main facts summarised in a single chapter for reference at any moment.

The important bearing which crystal research is now daily more and more assuming towards the progress of our knowledge of the nature of the chemical atom, and the definite aid it is offering towards the solution of that fundamental problem, and particularly the assistance it is already affording towards forming a judgment as to the two main rival theories of atomic structure now under discussion, together with the probability that its aid will

eventually be decisive in arriving at the truth and sifting out the fallacious elements, render the present a specially favourable moment for such a brief review of the subject as is afforded in this little book.

Every effort has been made to keep down the cost of the book, so as to render it available for as large a circle as possible. But those who become deeply interested in the subject, and desire more details, especially of the instruments used in both the researches which are described and in the practical work in general Crystallography, may refer to the author's larger work, "Crystallography and Practical Crystal Measurement," 2nd edition in 2 Vols., also published by Messrs. Macmillan and Co.

A. E. H. TUTTON.

*Cambridge,
24th October, 1925*

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CRYSTALLINE FORM AND CHEMICAL CONSTITUTION

INTRODUCTION

THE fact that each and every definite chemical substance, element, or compound which solidifies has its own crystalline form, except it crystallise with perfect cubic symmetry, and that even then it possesses its own crystallographic physical properties, must of necessity be of prime importance to chemistry. For long the study of the physical properties of crystals has also formed one of the chief branches of physics, so that a knowledge of the main facts of crystallography is essential to a thorough study of either chemistry or physics. It is true that a few substances crystallise in two or even (very rarely) in three or more forms, that is, are polymorphous. But these are only the exceptions that prove the rule, and the different forms are unlike those of any other substance. In these cases each form has a temperature range of stability, so that its life-history is confined within certain temperature limits, and there is a more or less definite temperature of transformation of one form into the other. Moreover, on fusion, solution, or volatilisation, both or all varieties afford the same liquid or gaseous molecules, single molecules which are identically similar, and are free to roll over each other if liquid, or to roam at will in the space in which they are confined if gaseous.

To go further, as showing that constitution as well as

empirical chemical composition is important, in reference to crystals, it is a fact that isomeric substances have quite different crystalline forms, their different constitution, although their empirical formula is the same, determining this most absolutely. For, as every chemist knows, two true isomers are really different chemical substances.

The fact of the specific crystallisation of every definite chemical substance rules more generally and universally in Nature than has ever hitherto been supposed. For X-ray analysis, a product of these later days, has shown that practically every solid substance composed of a definite chemical element or compound does crystallise, the substances which are truly amorphous and absolutely non-crystalline solids being very few and rare indeed, so rare that only a very few gelatinous substances have proved to X-rays to be non-crystalline. Most of the so-called colloids have been found to be sub-microscopically crystalline, even the finest colloidal gold, for instance, that gives the purple "solutions" that never in our time deposit their gold particles, having been shown to consist of extraordinarily minute yet nevertheless perfect little gold crystals of exquisite cubic structure.

It will be generally admitted as incontestable that the essence of a crystal is regularity of internal structure, stereotyped in the solid state of that particular substance, and this is actually caused by the definiteness of the chemical composition. How delighted a research chemist is when, on discovering a new compound, he finds it to crystallise well. Why is this? Because he realises that he has indeed secured a really definite new body, and in a state of practical purity. To see the crystals deposited from his solutions in the morning, after leaving them very doubtfully overnight, is a real joy to him. For the crystallised solid is either a chemical element, in which case it is built up of exactly identically similar atoms,

or it is a definite chemical compound composed of identically similar molecules of fixed chemical composition and constitution, all of them having the same number of elementary atoms of the different chemical elements present combined together in a similar manner.

Now these molecules may be arranged either all parallel to each other, a single chemical molecule being thus a kind of unit brick of the crystal edifice; or it may take a small group of two, three, or four, rarely more, chemical molecules to form the unit brick, the regular repetition of which throughout the structure builds up the crystal. In the latter event, the two, three, or four molecules composing the brick-group are not necessarily or even usually parallel to each other, but are in any case similarly mutually arranged, in accordance with the same definite scheme of symmetry, in all the groups, throughout the whole crystal. Going deeper into the structure, where chemical compounds and not single chemical elements are concerned, the details of the crystallography are determined by the mutual arrangement of the atoms of the two or more elements forming the compound, and if the "brick" is a group and not a single molecule, by the mutual arrangement also of the molecules composing the group.

In considering crystallography from the chemist's point of view we have the salient fact before us, as the product of modern chemistry, that an immense amount of information has now been acquired concerning the constitution of the molecules of the vast majority of chemical compounds, even complicated ones containing many atoms. And there is now much evidence that this molecular constitution, so clearly revealed both by pure chemistry and by the methods of physical chemistry in the cases of the liquid and gaseous states of the substance, goes likewise more or less intact into the solid state on crystallisation of the compound. That is to say, whatever symmetry

the chemical molecule possesses is operative in the crystal, and assists in building up the symmetry of the crystal, which is usually of a higher degree than that of the molecule itself. This interesting fact has only been definitely proved within the last few years.

When one remembers the great interest evoked when Wislicenus of Würzburg first led the way in stereochemistry, one wonders what that far-seeing and enthusiastic chemist would have thought of the "travail of his soul" could he but see the position to-day, and realise the immense advance which has been achieved.

Before we can go further into the relationship between crystal structure and chemical composition and constitution, however, it is necessary to review the main facts now established of pure crystallography, in order to clarify our ideas. It is an excellent moment in which to do so, for the use of X-rays during the last decade in the investigation of crystal structure has confirmed these facts, already made known by crystallographers, in the most perfect manner possible, so that we can feel certain that we are now on firm and assured ground.

CHAPTER I

THE MAIN FACTS OF CRYSTALLOGRAPHY

1. *To each Substance a Specific Form.*—The original principle, formulated by “the father of crystallography,” the Abbé Haüy, in the year 1782, was that “every single substance, definitely chemically constituted, possesses its own crystalline form.” This was intended further to mean that “the angles between the faces of this form are peculiar and special to the substance.” We must add to this, from later knowledge, “unless it be of cubic symmetry.” For the perfect symmetry of the cubic system itself determines the angles of the cubic forms, which are, therefore, invariable. We can also truthfully add, which substantiates Haüy even for cubic substances, “and, whatever the symmetry, even if cubic, is endowed with its own crystallographic physical properties, such as crystal density, optical refraction, elasticity, and electric constants.”

The facts above stated between inverted commas are now established without fear of contradiction. Even if the substance be polymorphous, the two or more forms are unlike that or those of any other body.

2. *Angular Magnitude and Crystal Elements the only safe Criterion of Form.*—Fortuitous relative development of the crystal faces, giving rise to very different appearances of specimens of the same substance from different sources, due to difference in environment conditions, is immaterial. For instance, the two crystals of ammonium ferrous sulphate, shown one inside the other in Fig. 1, look quite different, yet are built up of the same faces.

The only sound criterion of form is afforded by the magnitudes of the interfacial crystal angles, and the "crystal elements" which are or can be calculated therefrom. By "crystal elements" are meant the relative lengths and mutual angles of inclination of the three imaginary axes, which are supposed, for convenience of geometrical description of the crystal, to run from the imaginary centre of the crystal in the three directions of space. In practice they are taken parallel to the edges of intersection of three primary pairs of parallel faces, three mutually at right angles, if such are developed, or as near thereto as possible if the type of symmetry be not rectangular,

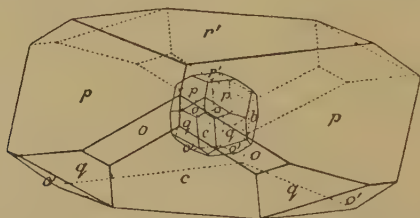


FIG. 1.—Two Crystals of Ammonium Ferrous Sulphate.

such as the faces a , b , and c of Fig. 2. Their lengths are determined by their intersection with the most important, primary, fourth face (PQR, face o , of Fig. 2) inclined to all three axial planes, or by two faces each inclined to two axial planes, complementarily. The vertical axis is always known as the axis c , and of the two horizontal or lateral axes a and b the latter runs from side to side and the a -axis from back to front. The axial ratios are expressed in terms of $b = 1$. For instance, the axial ratios of the triclinic crystals of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, are $a : b : c = 0.5715 : 1 : 0.5575$, and the axial angles are $\alpha = 82^\circ 16'$, $\beta = 107^\circ 26'$, $\gamma = 102^\circ 40'$; α is the angle between the axes b and c , β is that between a and c , and γ is the angle between a and b . This will be clear from Fig. 2.

3. *Constancy of Crystal Angles.*—The interfacial angles of the crystals of the same substance are absolutely constant, any slight variation being only due to rapid or disturbed crystallisation, as from solutions in the highly supersaturated condition known as “labile,” or from solutions in the less supersaturated state termed “meta-

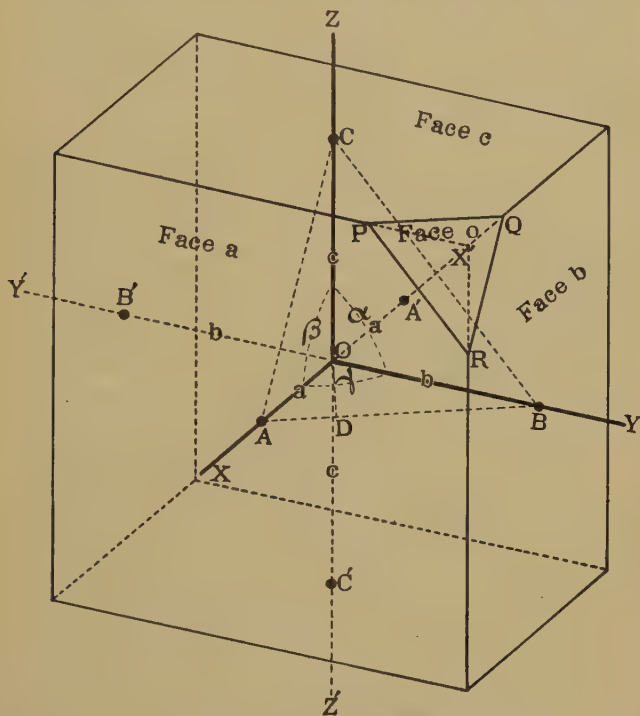


FIG. 2.—Crystal Axes and Primary Planes.

stable” which have been subjected to physical disturbance (see page 86). Crystals grown from metastable solutions under ideal undisturbed conditions afford interfacial angular measurements on the goniometer identical to a single minute of arc.

4. *Crystal Faces true Planes.*—The faces of such perfectly grown crystals are true planes, in the highest optical sense. They afford signal-images of the goniometer colli-

mator's signal-slit which are both brilliant and single, ideal for adjusting to the telescope cross-wires, especially as the slit employed is broad at its top and bottom ends, so as to pass ample light, and very narrow in its central part, for accurate allocation to the vertical cross-wire.

5. *Limitation of Faces to those with Rational Indices.*—The number and character of these truly plane faces are limited by the fundamental law of crystallography, that of "Rational Indices," or, as it is likewise called, the "Law of Rational Intercepts" or of "Anharmonic Ratios," or the "Zone Law." The fact which it expresses is that, having chosen the axial facial-planes and the fourth "parametral" inclined facial plane defining the axial lengths, as described under the preceding section 2, then the intercepts on these same three axes made by any other face on the crystal, compared with the standard lengths made by the parametral face as expressed in the axial ratios, will be "rational" whole numbers, that is, exact whole integers, usually small, such as 2, 3, 4, 5, 6, rarely more, no fractional parts being afforded.

These small whole numbers representing the relative intercepts on the axes serve, indeed, to indicate the position of the face. But it is found more convenient, for the purpose of obtaining a very short label or "symbol" for the face, not to use these whole number intercepts, but their inverse values, the well-known "Millerian Indices," given to us by Prof. W. H. Miller (Professor of Mineralogy at Cambridge from 1832 to 1881) in 1839. These latter are likewise small whole numbers and are such that, if O be the imaginary centre of the crystal, OA , OB , OC the standard lengths intercepted on the axes a , b , c by the parametral fourth face, and OH , OK , OL the lengths intercepted by the new face under discussion, then the Millerian indices of this fifth face are h , k , l , rational whole numbers such that $h = \frac{OA}{OH}$, $k = \frac{OB}{OK}$,

$l = \frac{OC}{OL}$. They are written in brackets, thus (hkl) ; for instance, (312) .

If the face be parallel to an axis, the index corresponding is a 0. Thus (120) is a face parallel to the vertical axis c .

6. *Zones and the Anharmonic Ratio of their Faces.*—One of the most interesting facts about crystals, and of the greatest practical use in goniometry, is that their faces lie in zones. The edges of intersection of all the faces of a zone (that is, of every successive two faces) are all parallel to each other and to the imaginary zone axis. If any two adjacent faces are adjusted parallel to the goniometer axis, so that the signal-images reflected from them can be brought to the cross-wire centre of reference in the field of the telescope by the rotation of the goniometer axis, then all the other faces of the zone are also thereby automatically adjusted, so that the images of the collimator signal-slit, reflected from all the other faces in succession, will also pass the reference centre of the telescope field when the goniometer axis is further rotated, the goniometer axis and the zone axis being then identical in direction.

The plane perpendicular to all the interfacial edges of a zone is the "zone plane." Fig. 3, the so-called "Spherical Projection," in which the crystal is concentrically surrounded by a sphere, and normals are drawn to all the faces, shows the "zone circles" in which the zone planes cut the sphere, and the "facial poles" in which the normals intersect the zone circles. Obviously these poles define the positions of the faces; for the angle between two faces actually measured on the goniometer is that between the normals to the two faces, that of the intercepted arc of the zone circle.

The practically immensely useful "Stereographic Projection" is just this spherical projection, projected on the equatorial plane from the eye placed at the north

pole. The equatorial plane is the circle bounding the stereographic projection, and all the other zone circles appear as circular arcs or diametrical straight lines. (For examples see Figs. 39 and 46.)

Further, one of the fundamental principles of crystallography, intimately bound up with the Law of Rational Indices, is a simple mathematical connection which exists between the positions of the various faces in the zone and their indices. It is known as the "Anharmonic Ratio of Four Poles in a Zone." It may be stated briefly thus :

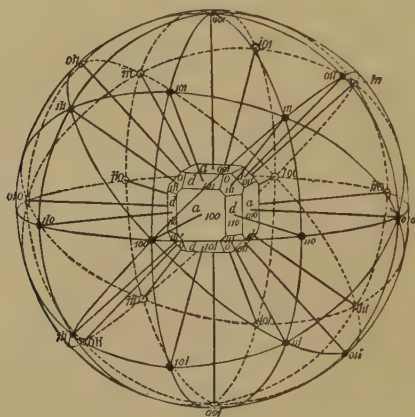


FIG. 3.—The Spherical Projection.

"If a , b , c , d be four faces in a zone, the double-ratio (anharmonic ratio) of the sines of the angles between them is a rational number, which is expressed by the corresponding double-ratio of the indices of the four faces." Or otherwise expressed : "The anharmonic ratio of the sines of the angles between four faces of a zone is equal to the anharmonic ratio of their indices."

Now the latter (the indices side of the equation) works out to a simple low integer-number, or a simple fraction with a low integer for numerator and another for denominator. This must be so, as the indices themselves are rational whole numbers, and their anharmonic ratio

is simply found by cross-multiplying them in pairs, in the same order as the angles are taken. The left or angle side lends itself to easy calculation, and in the event, commonly happening, of one of the angles being a right angle simplifies to the ratio of two tangents. If one of the angles has been measured, and the other is to be calculated, the product of an integer (1, 2, 3, or 4, rarely more) and the tangent of a known angle will give the tangent of the required angle, and hence from a table of tangents the angle itself. Or if both angles are known, the indices can be calculated.

Even in the general case, with no right angle, if we know the positions of any three faces in the zone, and know or assume all the indices, that of the fourth face may readily be calculated. And contrariwise, if the angles are all known we can find the indices of any one (considered as the fourth) of the faces, those of the other three faces being known. Hence, the principle of the anharmonic ratio is of the utmost importance.

7. *Crystals Classified by Symmetry into Seven Systems and Thirty-two Classes.*—The symmetry displayed by the disposition of the crystal faces is that of one of “The Thirty-two Classes of Crystals,” which have been distinguished by crystallographers, and which group themselves into “The Seven Systems of Crystal Symmetry” (the Cubic, Hexagonal, Tetragonal, Trigonal, Orthorhombic, Monoclinic, and Triclinic), according to the main type of their symmetry and the nature of the “Crystal Axes” which are conveniently used to describe them, on the lines stated in section 2. While it is sometimes difficult to be quite certain of the particular class to which a crystal should be allocated, there is usually no difficulty in determining the system to which the crystals of a substance belong when the observations are extended to a considerable number of crystals and not confined to a single one, and the optical properties are also observed.

The criteria of symmetry, used in the classification of crystals, are planes and axes of symmetry. The latter are of hexagonal, tetragonal, trigonal, or digonal type, which are respectively such that if rotation of the crystal occur around the axis for 60° , 90° , 120° , or 180° , the appearance of the crystal is the same as before the rotation occurred. A plane of symmetry is an imaginary plane passing through the centre of the crystal (imagined to be ideally developed), and dividing the latter into two equal halves which are the mirror-images of each other. The "Centre of Symmetry," although frequently spoken of to indicate that the crystal has pairs of parallel faces, one equally on each side of the centre, is not a true "Element of Symmetry," as rotation for 180° or for 60° around a digonal or hexagonal axis of symmetry, followed by reflection across a plane of symmetry, produces the same effect.

The older idea that the classes of any system possessing fewer than the full elements of symmetry possible to the system (this perfect class being known as the "Holo-hedral," a term it is convenient to retain) have certain symmetry elements suppressed, and which gave rise to the terms "Hemihedral" and "Tetartohedral" for such classes, is now replaced by the more scientific view that each class possesses its own definite elements of symmetry, special and peculiar to it, quite independently of how many symmetry elements are possible to the group-System. So that Symmetry and not whole or partial Development is the criterion of classification.

The Cubic System, of highest symmetry, is defined by three equal imaginary crystal axes at right angles to each other, parallel to the edges of the cube, the axial planes being parallel to the cube faces. The highest class, the "holohedral," representing its full symmetry, class No. 32, possesses the highest symmetry possible to crystals, having no fewer than twenty-two elements of

symmetry, namely, nine planes and thirteen axes of symmetry. The primary parametral "form" $\{111\}$, defining the relative lengths of the axes (in this case identical), is the octahedron, the interfacial edges of which join the ends of the axes. The most general form, differently inclined to all three axes, is the hexakis octahedron, the two commonest representatives of which have the indices $\{321\}$ and $\{421\}$. There are four other definite solid polyhedra belonging to the class besides the three already mentioned, namely, the rhombic dodecahedron $\{110\}$, of which, like the cube and the octahedron, there is only one; the icositetrahedron, of which there are two com-

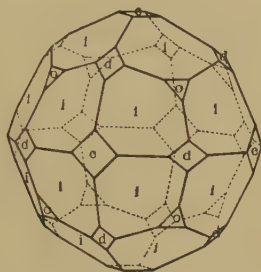


FIG. 4.—Combination of Cubic Forms.

mon representatives, $\{211\}$ and $\{311\}$, the two last indices being always alike; the triakis octahedron, represented by $\{221\}$ and $\{331\}$, the two first indices being always alike; and the tetrakis hexahedron, $\{210\}$ or $\{310\}$. All these polyhedra have definite invariable angles, determined by the symmetry itself. Fig. 4 shows a combination of the cube, octahedron, rhombic dodecahedron, and icositetrahedron $\{211\}$, the latter predominating. Fig. 5 represents the hexakis octahedron $\{321\}$.

There are four other classes in the cubic system; the lowest, class 28, possesses only the minimum elements of cubic symmetry, having no planes of symmetry, but seven axes of symmetry, three being digonal and coincident with the crystal axes, and four trigonal. The three

axes of symmetry. The intermediate five classes possess intermediate stages of symmetry.

The *Orthorhombic System*, also called *Rhombic*, is likewise defined by three rectangular crystal axes, but all three are unequal. The axial-plane form, the rectangular rhombic prism, is really composed of three separate "forms," each parallel pair of faces being a separate form, $\{100\}$, $\{010\}$, and $\{001\}$. The highest class, No. 8, has three digonal axes of symmetry, coincident with the crystal axes, and three planes of symmetry coincident with the crystal axial-planes. Besides this holohedral

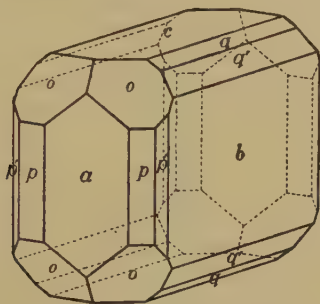


FIG. 7.—Rhombic Crystal of Cæsium Sulphate.

class 8 there are two other classes, 7 and 6. The latter the lowest rhombic class, has only the three axes of symmetry with no planes of symmetry. No. 7 has one digonal axis, counted as the vertical crystal axis, and the two planes of symmetry which intersect in it. Fig. 7 is a drawing of a rhombic crystal of cæsium sulphate, which shows all the primary forms; a is $\{100\}$, b is $\{010\}$, c is $\{001\}$, p is $\{110\}$, q is $\{011\}$, and o is $\{111\}$.

The *Monoclinic System* is defined by three imaginary crystal axes of unequal lengths, two being inclined to each other at any angle other than 90° (but usually chosen as fairly near as there is a face developed), with the third perpendicular to them and normal to their plane. Its highest class, the holohedral class 5, possesses a plane of

symmetry, that containing the two inclined crystal axes, and a digonal axis of symmetry perpendicular to it. Class 4 has only the digonal axis, and no symmetry plane, while class 3 has the symmetry plane without the digonal axis.

The angle between the two inclined axes is important, being a "crystal element," and is known as the axial angle β (for the digonal symmetry axis is taken as coincident with the crystal axis b), and requires to be stated along with the axial ratios.

The axial-plane form, the oblique rectangular prism, is composed of three forms as in the rhombic system, each

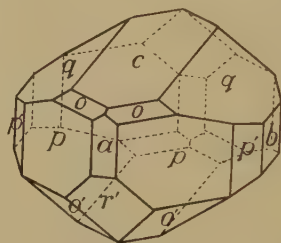


FIG. 8.—Monoclinic Thallium Cobalt Sulphate.

parallel pair of faces being a separate "form." Fig. 8 is a drawing of a monoclinic crystal of thallium cobalt sulphate, showing all the primary forms; a is $\{100\}$, b is $\{010\}$, c is $\{001\}$, p is $\{110\}$, q is $\{011\}$, o is $\{111\}$, and o' is $\{\bar{1}11\}$, the primary bipyramid being now composed of two forms, making up together the equivalent of the octahedron.

The Triclinic or Asymmetric System is defined by three unequal and non-rectangularly and unequally inclined crystal axes. Of its two classes, Nos. 1 and 2, the latter possesses a centre of symmetry, so that every face has a parallel fellow, and the two constitute a separate "form," but otherwise no symmetry is apparent. No. 1 class has no symmetry whatever, there being no parallel faces. In this system, as there are no right angles, all

three interaxial angles are crystal "elements," and have to be stated along with the axial ratios. Fig. 9 represents a triclinic (class 2) crystal of copper sulphate measured by the author. Every pair of parallel faces is a separate form, and a , b , and c are the primary forms $\{100\}$, $\{010\}$, and $\{001\}$.

The use of the term "form" in inverted commas, to signify that the crystallographic technical meaning is intended, will have more or less indicated that a "form" in this restricted sense means the collection of faces, or

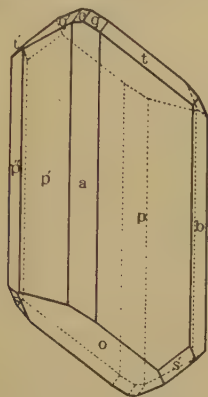


FIG. 9.—A Triclinic Crystal of Copper Sulphate.

the single face (as often happens in the classes of lower symmetry than the holohedral in the three lowest systems), having the same value and relationship to the symmetry. The degree of symmetry thus determines the number of faces which shall go to a "form," and in the most general cases of forms the faces of which are inclined to all three crystal axes, the number varies from the 48 faces of the hexakis octahedron in class 32 down to a single face in the triclinic class 1. Moreover, all the faces of this latter class, and two certain types of faces in the monoclinic classes 3 and 4, are separate forms.

The Trigonal System is defined by three equal and equally inclined axes, but their angle is not 90° (except

as a very rarely occurring special case). Its lowest class, No. 16, of the seven which belong to it has only one symmetry element, the essential trigonal axis of symmetry.

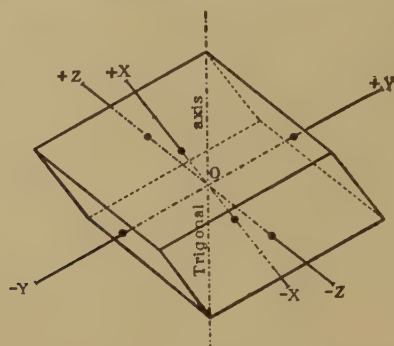


FIG. 10.—The Rhombohedron and Trigonal Axial System.

The axial-plane form is the rhombohedron, resembling a cube flattened or extended along a diagonal, which is the upright trigonal axis of symmetry. The highest class, No. 22, possesses, in addition to the trigonal vertical axis, three symmetry planes intersecting in it at 120° ,

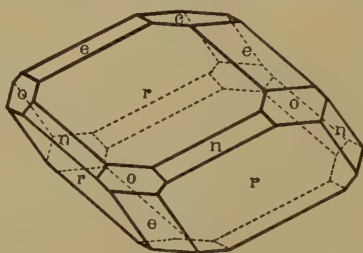


FIG. 11.—Trigonal Crystal of Calcite.

and an equatorial plane of symmetry with three digonal axes of symmetry lying in it, at the intersections with the three vertical planes of symmetry. Fig. 10 shows the rhombohedron and its axial system, and Fig. 11 an actual crystal of calcite, a combination of the hexagonal prism $n\{10\bar{1}\}$ with three different rhombohedra, of which r is the primary one $\{100\}$, which largely predominates.

The *Hexagonal System* is peculiar in having three equal crystal-axes inclined at 60° to each other, in the horizontal plane, and a fourth crystal axis, the vertical one

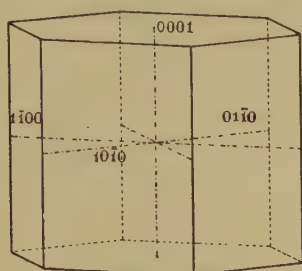


FIG. 12.—First Order Hexagonal Prism.

coincident with the essential hexagonal axis of symmetry, and perpendicular to the other three crystal-axes. Its lowest class, No. 23, has no other element of symmetry than this hexagonal axis. Its highest class, No. 27, has

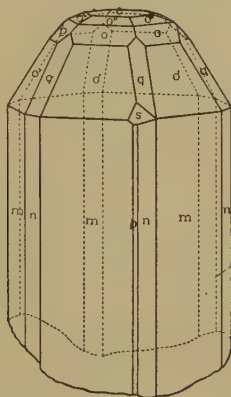


FIG. 13.—Hexagonal Crystal of Apatite.

in addition six planes of symmetry intersecting in the hexagonal axis, and an equatorial plane of symmetry with 6 digonal axes lying in it. The axial-plane form is the hexagonal prism of the first order, but it does not include the pair of parallel end-faces perpendicular to the prism faces, these basal plane faces being a separate

“form.” It is shown in Fig. 12, and Fig. 13 represents a crystal of apatite measured by the author, which shows these primary forms $\{10\bar{1}0\}$ and $\{0001\}$ combined with the hexagonal prism of the second order n , $\{11\bar{2}0\}$ and several hexagonal pyramids, including the primary one $\{10\bar{1}1\}$.

8. *Great Use of Optical Properties in Crystal Classification.*—The optical properties, especially the refractive index or indices, and the behaviour of the crystal in parallel and convergent polarised light, are of great assistance in fixing the system. In any case they at once discriminate between three cases. (a) A cubic

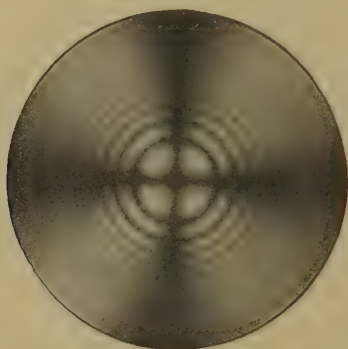


FIG. 14.—Uniaxial Figure in Convergent Polarised Light.

crystal is discriminated by its “isotropism,” lack of double refraction and possession of only a single refractive index. (b) A hexagonal, tetragonal, or trigonal crystal is recognised by its “Uniaxial” interference figure, a rectangular black cross and circular concentric spectrum rings, in convergent polarised light, as shown in Fig. 14, when a plate perpendicular to the hexagonal, tetragonal, or trigonal axis is examined in the polariscope or polarising microscope; and also by its single refraction along this axis and double refraction in all other directions; and by the possession of two refractive indices corresponding to light vibrations along and perpendicular to the axis. And (c) an orthorhombic, monoclinic, or triclinic crystal

is indicated by its "Biaxial" character, exhibiting in convergent polarised light the well-known interference figure of two optic "eyes" or directions of apparent single refraction, surrounded by rings and lemniscates in spectrum colours and connected by a black bar crossed rectangularly by a broader black band at the midway position between the two optic axes, when a plate perpendicular to the bisectrix of the angle between the optic axes is examined, as illustrated in Fig. 15; and also by the fact that the

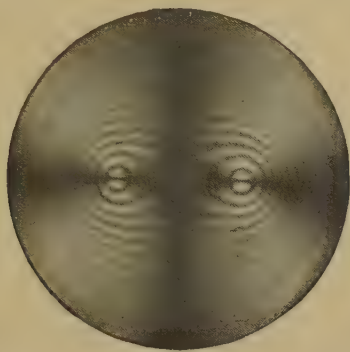


FIG. 15.—Biaxial Figure in Convergent Polarised Light.

crystal possesses three refractive indices, corresponding to the vibrations of light along the acute bisectrix just referred to, along the obtuse bisectrix at right angles to the acute one, and along the direction perpendicular to the plane of the optic axes and their bisectrices.

If the optical examination has indicated that the crystal is uniaxial, the goniometry will readily settle whether it be hexagonal, tetragonal, or trigonal. If a biaxial system be indicated by the optics, it will be orthorhombic if the three perpendicular directions just referred to in connection with the refractive indices and the interference figure (the two bisectrices and the normal to their plane) are identical with the three crystal axes already shown by the goniometry to be all mutually rectangular. If the goniometry indicated a possibility of monoclinic

symmetry, one of those three perpendicular optical directions will be identical in direction with the single axis of monoclinic symmetry, the other two being free to be anywhere in the plane perpendicular to that axis, so long as their mutual rectangularity is preserved. If no symmetry has been goniometrically indicated, and no exact correspondence of any one of the three optical perpendicular axes with any crystal axis is indicated by the optical examination, then the crystal must be, provisionally at any rate, set down as triclinic. In this manner, and by many other subsidiary aids, can the optical examination assist in the allocation of a crystal to its proper system. If, moreover, the crystal should show the interesting optical property of rotation of the plane of polarisation, it will be possible usually to allocate it also to its particular class in the system, for it must be a class possessing no plane of symmetry, the condition for optical activity.

9. *A Space-lattice the Foundation of Crystal Structure.*—The explanation of the Law of Rational Indices is that crystal structure is essentially that of a lattice in space, a three dimensional "Space lattice," such as that of most general (triclinic) type shown in Fig. 16, the unit cells of which, the "bricks" of the edifice, are real tangible objects of definite size, although submicroscopic so that a crystal face appears polished and continuous. It is now definitely proved that these individual cells are each occupied either by a single chemical molecule, or more frequently by a small group of two, three, or four (rarely more) chemical molecules of the substance crystallised. It is the type of space-lattice which the substance develops, the nature and the mode of repetition of the unit cell, that determines the system of symmetry of the crystal. There are fourteen types of space-lattice, which fall into the seven systems. The crystal-class and the finer details of the structure are determined by the arrangement of the atoms in the cell, that is, in the molecule or

group of molecules "occupying" the cell. If we consider the atoms as points, there are 230 modes of arranging the points, possible to crystals, all the modes falling into accord with one or other of the 32 classes of crystals.

Bravais established the fact that there are only 14 space-lattices, three possessing parallelepipedal cells of cubic symmetry, two with tetragonal cells, one with

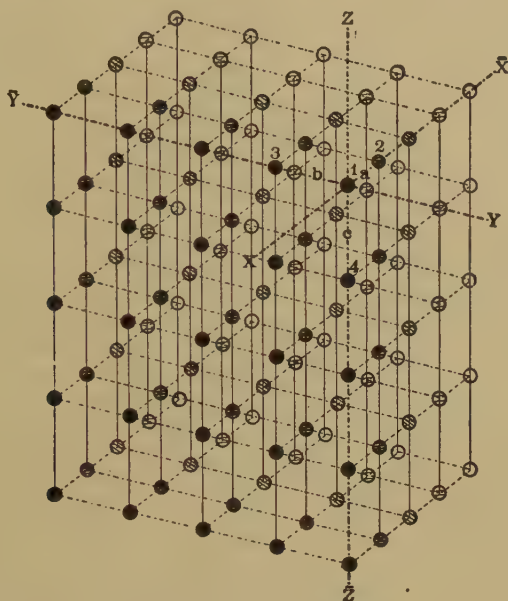


FIG. 16.—Space-Lattice.

trigonal-hexagonal cells, one with trigonal-rhombohedral cells, four with orthorhombic cells, two with monoclinic cells, and one with triclinic parallelepipedal cells.

Sohncke described 65 of the more commonly occurring and more fundamental regular point-systems, and Schoenflies, Barlow, and Fedórov independently worked out the remaining 165 of the 230. The 14 space-lattices are not extra to the 65 or 230 point-systems, but form the skeleton, as it were, the points being grouped around the nodes of the space-lattice; and in certain cases the space-lattices

are special cases of the point systems, to which the latter simplify or reduce. The 65 Sohnckean regular point-systems involve only geometrical "cover-operations" or "coincidence-movements" of the first order, simple rotations or translations, by the operation of which the same appearance is restored. The further 165 types of homogeneous structure involve also the more complicated second order kind of "coincidence movements," about a centre of symmetry, a mirror-reflection plane, gliding mirror-reflection plane, or mirror-axis, operations which result in the production of the mirror-image body instead of apparent identity or coincidence with the original. These more complicated point-systems may be grouped about the 65 regular point-systems of Sohncke.

Quite recently W. T. Astbury and Miss K. Yardley, and also in America R. W. G. Wyckoff, have simplified the subject by showing that while many of the more complicated of the 230 point-systems admit of some latitude in regard to the position of some of the points, in the case of actual crystals the atoms, represented by these points, are really limited to very few possible positions, and they have published descriptions of the only possible arrangements of the atoms in such cases. Wyckoff gives them as the analytical co-ordinates of equivalent points; Astbury and Miss Yardley have gone further and given diagrams of the arrangements for all the 230 point-systems or "space-groups," together with full descriptions and the number n of asymmetric molecules required to produce the structure in each case, and also of n/p if the molecule has symmetry of the order (symmetry number) p . Hence, the structure of any substance, as determined from crystallographic measurement or when revealed by X-ray analysis, or best of all by both methods combined, must conform to one or other of these definite types which have been catalogued and figured in the drawings.

10. *Topic Axial Ratios as Relative Measures of Cells.*—In the cases of substances so similarly constituted as to be constructed on the plan of the same space-lattice it is possible to get relative measures of the volume and edge-dimensions of the unit cells of the space-lattice. This is done by combining the “crystal elements” (the ratio of the axes, $a : b = 1 : c$ and the axial angles α, β, γ) with the molecular volume V , which is found by dividing the molecular weight of the substance by the density of the crystal, which requires to be very accurately determined for the purpose. These three relative measures thus obtained are known as the “Topic Axial Ratios,” or “Molecular Distance Ratios,” and are symbolised by λ, ψ , and ω . (See also page 92.)

11. *Absolute Measures of Cells by X-Rays.*—The analysis of crystal structure by X-rays, by the spectrometric method of Sir William H. Bragg, has now afforded absolute measures of the volumes and edge-dimensions of the space-lattice cells of a large number of substances, including some for which the relative measures had been obtained by the author by the method of the preceding section 10. In these cases the agreement has proved excellent, the absolute values bearing precisely the relations indicated by the relative values.

12. *X-Rays as Analysts of Crystal Structure.*—The basis of the wonderful method of unravelling crystal structure which we owe to Prof. von Laue is the fortunate fact that the wave-lengths of X-rays are of the same order as the sizes of chemical atoms, both being of the order 10^{-8} centimetre. X-rays are, in consequence, reflected or diffracted by the planes of atoms regularly succeeding each other at fixed spacings in the crystal structure, on a similar principle to that of a diffraction grating or echelon spectroscope. The Laue photographic method uses a bundle of X-rays of different wave-lengths corresponding to white light, and the photograph shows a spot for each

parallel set of planes of the space-lattice, corresponding to the accumulated reflections from that set. Consequently there is a spot for each face which comes within the purview of the rays, and indeed from all possible faces within range, not only those actually developed. The pattern of the Laue spot photograph, that is, formed by the whole collection of spots, corresponds to the symmetry of the crystal. It should be very clearly understood that

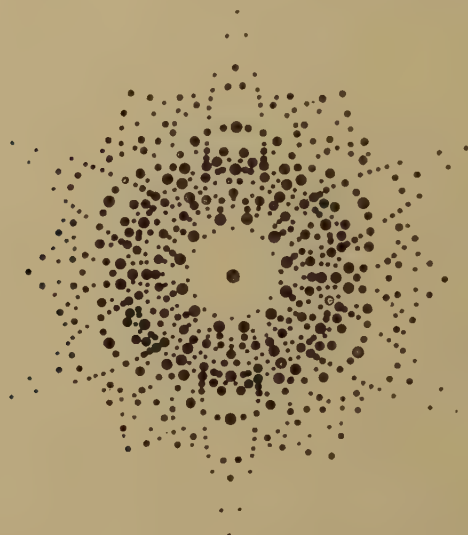


FIG. 17.—Laue X-Ray Photograph of Beryl.
(Rinne.)

it is not reflection of X-rays from the actual crystal faces, but from the sets of innumerable parallel planes, corresponding to faces, in the interior of the crystal, reflection from a single plane of atoms, such as that corresponding to the actual polished surface of the face, being too feeble to afford any effect on the photographic plate. A Laue photograph of hexagonal beryl is reproduced in Fig. 17, and will illustrate how clearly the symmetry is brought out, and the wonderful detail of the space-lattice structure and large number of different planes of atoms, all corre-

sponding to possible faces, which are revealed by the spot-pattern.

13. *Determination of Nature and Dimensions of Space-Lattice Cells.*—The later X-ray method known as the "Spectrometric," which we owe to Sir William H. Bragg, locates the direction of the reflected X-rays by means of an "ionisation" tube which replaces the telescope of a

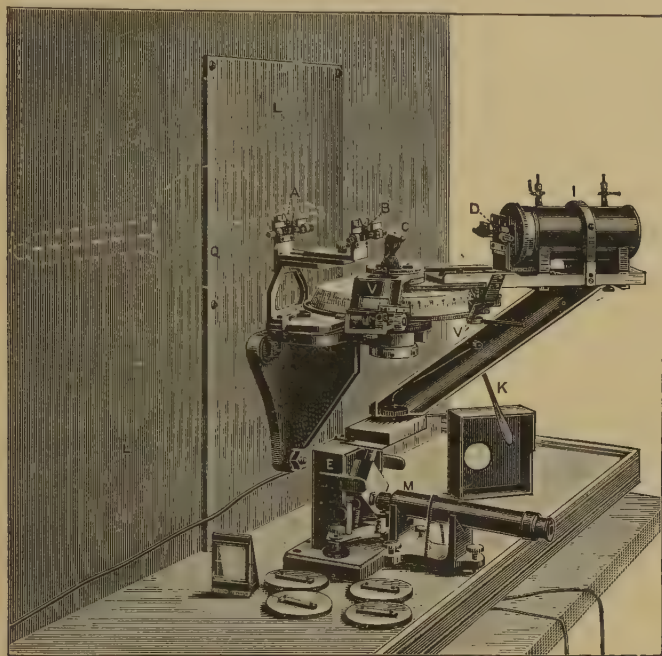


FIG. 18.—The Bragg X-Ray Spectrometer.

spectrometer; it is filled with sulphur dioxide or methyl bromide and is provided with an electroscope or equally delicate string electrometer, enabling not only the first order reflection but the others up to the fifth to be measured. The whole apparatus is shown in Fig. 18. It also enables not only the angles of reflection but the intensity to be determined, and from the relative intensity of the different orders of spectra reflected to obtain valuable information as to the nature and composition of the planes of atoms

affording the reflection or diffraction; that is, whether the successive planes of atoms are similar or different ones, composed of the same or different atoms of different elements. For it was roughly found that atoms of different chemical elements differ in the intensity of their reflection, in a more or less proportionate manner to their mass or atomic weight and number. Otherwise stated, the amplitude of the waves reflected by each net-plane is nearly proportional to the total mass of the atoms lying in that net-plane. If the atoms composing the successive planes of a set are all of the same elements, and identically arranged, there is a regular order of reflection intensity for the five orders of X-ray spectra which are generally observed, but this order, a rapidly diminishing one as we pass from spectrum 1 to spectrum 5, is altered if the alternate planes, or every third plane, etc., differ in composition.

The great importance of the Bragg method is that it affords an exact, absolute, measure of the spacing of the successive planes, and as this can be done so easily for all the three principal planes it means the absolute determination of the edge-dimensions of the unit-cells of the space-lattice, as well as their volume. The basic formula, now so well known, is

$$n\lambda = 2d \sin \theta,$$

in which n is the order of the spectrum, λ the wave-length of the "monochromatic" X-rays, θ the angle of their "grazing" reflection (that is, the complement of the angle from the normal to the plane), and d is the spacing of the parallel planes. It will be observed that as the wave-length of the X-rays is an important factor the rays used must be as strictly "monochromatic" as is attainable, and this can fortunately be achieved by the use of X-ray tubes with certain specific metallic anti-cathodes, such as that of palladium, which affords the

specific radiation 0.584×10^{-8} cm. very strongly. This fact, the use of "monochromatic" rays, distinguishes the Bragg method from the photographic one of Laue.

A third method of experimenting was introduced by Debye and Scherrer, and independently by A. W. Hull, in which it was not necessary to use a good well-developed crystal, crystal powder being used instead, compressed into a small rod, the reflections being received in a concentric cylindrical camera; for among the heterogeneously arranged particles are many conveniently arranged to afford interpretable indications of the crystal structure. Sir William H. Bragg also afterwards used crystal powder in many cases, but spread and cemented on a plate, with his ordinary method, and also with a method in which the plate with the crystal powder is rotated, oscillated, about the convenient position. All these variations of X-ray methods lead either to similar or complementary results in the end, and it is of great advantage to employ all three methods, the Laue photographic, the Bragg spectrometric, and the powder method; for each has some advantage in some direction or other, and the use of all three affords wonderfully complete and well-confirmed information.

14. *The Number of Chemical Molecules in the Unit Cell.*

—In the simpler cases, such as those of binary compounds like the chlorides of sodium and potassium, NaCl and KCl, or those containing only three elements such as calcite CaCO_3 , the arrangement of the atoms of the different chemical elements is directly given by the X-ray results, and the structure thus appears as if it were of atoms and not of molecules, although of course the molecules are really there, as they were deposited from the saturated solution as such. These simpler cases have become referred to, probably not very accurately or advisedly, as "ionised crystal-structures." Yet in the face-centred cube of either rock-salt or potassium chloride,

and in the corresponding face-centred rhomb of calcite, four chemical molecules definitely go to compose this unit-cell of the space-lattice. But in the case of complicated compounds, such as those of organic substances like tartaric acid or naphthalene, what is directly revealed is the molecular arrangement, that of the space-lattice, the unit-cells of which are composed of one to four molecules; in the cases of both tartaric acid and naphthalene there are two chemical molecules, $C_4H_6O_6$ and $C_{10}H_8$ respectively, to each cell. The chemical molecule in these cases is very definitely present, and the exact way in which the two are arranged with respect to each other has been determined. Now as the molecule goes into the crystal with practically no change, the stereometric arrangement of its atoms, and its consequent chemical constitution, is a matter of immense importance, and if the arrangement of the atoms shows any elements of symmetry these must have an influence on, and indeed take part in, the crystal symmetry, and assist in determining the particular class of the system which is developed.

Nature in many cases builds up a crystal from a small number n of totally asymmetric molecules, as already shown. If for asymmetric molecules there are substituted molecules of p -fold symmetry, it may be only necessary to use n/p molecules to attain the same structure. Thus in the case of naphthalene only two molecules instead of four are required in the cell to give the observed symmetry, as the naphthalene molecule itself possesses two-fold symmetry. The symmetry of the molecule referred to is that of the molecule as it is in the crystal, and all the evidence goes to show that it is practically that of the free molecule in the liquid or gaseous state, no appreciable change or distortion of moment occurring during the settling into the crystal.

The actual number of molecules in the unit-cell of the space-lattice is found by comparing the product of the

volume of the cell (which in rectangular systems is the product of the three cell-edge dimensions) and the density (specific gravity), with the product of the molecular weight of the substance and the weight (mass) of the hydrogen atom (which is known to be 1.64×10^{-24} gramme). Either the two products will come out as identical within experimental error, or the former will be n -times the latter; n is then the number of molecules in the cell. Taking, for instance, the case of the rectangular unit-cell of potassium sulphate K_2SO_4 , which has four chemical molecules to the cell, the product of the cell-volume and the density was 1135×10^{-24} gramme, while the product of the molecular weight and the mass of the hydrogen atom worked out as 284×10^{-24} gramme, just one-fourth of the former product, corresponding to a four-molecule cell.

15. *Fedorov and Shearer's Principle*.—In the year 1922 G. Shearer worked out the number of asymmetric molecules per crystal unit-cell required to produce the symmetry of the 32 classes of crystals, and from the considerations given in the preceding section 14 deduced that the existence of fewer than this required number implied symmetry of the molecule itself. He then elaborated the following principle. “The number obtained by dividing the weight of the crystal-unit by the molecular weight is either equal to the symmetry number (the number of asymmetric molecules in the unit) or is a sub-multiple of it. In the latter case, the number obtained by dividing the symmetry number by the number of molecules is the symmetry number of the molecule.”

This principle has so far stood the test of experiment well. No case has been observed in which the number of molecules in the cell has been found to be greater than the symmetry number, as thus defined, but cases in which it is smaller, a sub-multiple, are common. Most of the complicated organic compounds which have been examined

by X-rays, for instance, where no symmetry is perceptible in the molecule, have been found to be of holohedral monoclinic symmetry, with a symmetry number four, and there are four molecules to a cell. Naphthalene and anthracene, having two-fold symmetrical molecules (there being a centre of symmetry), have only two molecules to the cell. In the case of tartaric acid, its symmetry number is only two, corresponding to the sphenoidal class of the monoclinic system, and there are two molecules to the cell; the molecules of tartaric acid, therefore, must be asymmetric, as we know they are from their optical activity, as regards symmetry planes and second order axes, which are certainly absent.

This principle of Shearer was really proposed by E. S. Fedorov in the year 1912. For he showed that $n = mp$, where n is the symmetry number of the crystal unit, m the number of molecules it contains, and p the symmetry number of each molecule. The rule should, therefore, be called "The Principle of Fedorov and Shearer." It is certainly one of great importance, and equally so to crystallographers and to chemists.

16. *The Three Crystallo-Chemical Entities.*—As regards the connection between crystal structure and chemical composition three things, quite distinct, have to be distinguished clearly. They are, (a) the crystal unit (the unit-cell of the space-lattice), (b) the crystal molecule or chemical molecule as it exists in the solid crystal, and (c) the chemical molecule as it exists more or less free in the liquid and gaseous states. The first is composed either of the second in its simple and single state or of two, three, or four and rarely more chemical molecules; the second may or may not be identical with the third, but it has been found so far that the difference, if there be one, is but small and very subsidiary, not affecting the actual linkage between the atoms, but possibly somewhat touching their actual disposition in space, as there

may be some slight distortion or compression when the molecule fits into the crystal edifice.

17. *The Sizes of the Atoms in Crystals.*—Finally, in this review of the facts of crystallography which it is necessary to have before us, a word is essential as to the sizes of the chemical atoms when they enter into crystal structures. From measurements of the closest approach to each other of the atoms in all the crystal structures which have been analysed by means of X-rays, W. L. Bragg has published a list, and a corresponding curve, reproduced in Fig. 19,

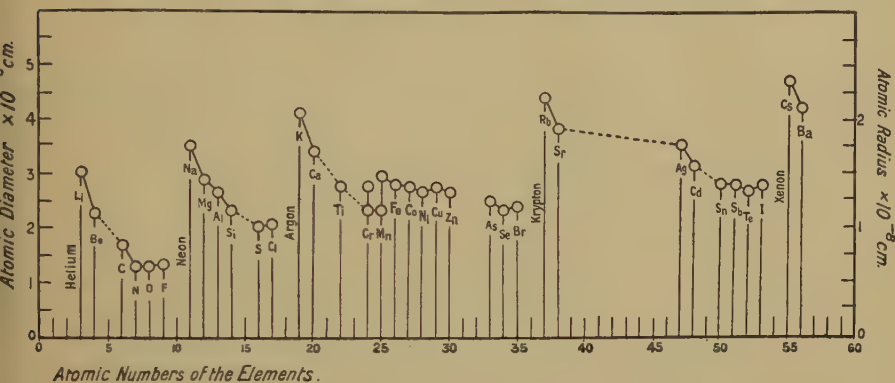


FIG. 19.—Curve of Atomic Diameters.

expressing the results graphically, of the diameters of the atoms of the various elements concerned in the structures investigated. These diameters may be regarded as the diametral dimensions of the outer shell of electrons of the atoms, or at least of the spherical surface of nearest approach to contact with other neighbouring atoms, the sphere of influence or atomic domain. This interesting curve is periodic, reminding one of the curve of atomic volumes of Lothar Meyer; the electropositive alkali metals occupy the maxima, which are themselves progressive, becoming higher as the atomic number of the metal increases, and the electronegative elements and the inert gases occupy the minima. It is probably too early yet to form a decisive opinion as to its general validity,

and it has been severely criticised by Wyckoff. Yet even he agrees that it represents the probable truth in the cases of isomorphous series, for the members of which the arrangement of the atoms and the type of structure is the same. There is clear evidence from the author's own researches that this so-called Law of Atomic Diameters holds in such series. It may be that, as with Topic Axial Ratios, when the type of structure is quite different the absolute dimensions of the atoms of the different elements may be somewhat altered, and thus not strictly comparable without some additional factor being introduced.

There can be no doubt, however, that atomic size does influence crystal structure, and the suggestion of Sollas, made so long ago as 1898, that the atomic volume of Lothar Meyer and Kopp was a governing consideration in the packing and stable arrangement of the atoms in crystals, may prove in the end to have not been very wide of the mark.

The interesting valency volume theory of Sir William H. Pope and Mr. W. Barlow, according to which the sizes of the various atoms in any one crystal structure were proportional to their chemical valencies, was another attempt, and one particularly important to chemists, to arrive at a general principle governing the mode of arrangement of the atoms in crystals, and the reason for the adoption of the particular homogeneous structure which any chemical substance affects as its stable solid form. That theory may now be said to be replaced—having done splendid work in calling attention to the subject, and before X-ray analysis was thought of—by the Law of Atomic Diameters of W. L. Bragg. And this, in turn, will require modification and perfection before it is generally accepted as representing the truth in all cases and for heterogeneous types of structure. As further research is in hand on the subject, it will be well to end this review at this point.

CHAPTER II

ISOMORPHISM

ROMÉ DE L'ISLE in the year 1772 appears to have been the first to have observed a fact, which proved to be the pioneer one in connection with the great subject of isomorphism, that the long-known double sulphates called alums, potash alum, ammonium alum, and iron alum, which potassium or ammonium sulphates form with the sulphates of aluminium and ferric iron, will readily grow together in mixed crystals or in overgrowths of one crystal on another. His observations were confirmed and extended by Le Blanc in 1784, Vauquelin in 1797, and by Gay-Lussac in 1816. The alums, however, crystallise in the cubic system, and their interfacial angles are therefore all identical in the different salts, being determined by the symmetry itself, no variation being possible. We now know their constitution to include a large quantity of water of crystallisation, and to be $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, in which the potassium, K, may be replaced by the ammonium radicle NH_4 or by the since-discovered additional alkali metals rubidium Rb and Cæsium Cs, or by thallium Tl in its thalious capacity; while the aluminium can be replaced by ferric iron or chromium, or by the later-discovered rarer elements gallium and indium. No question of the validity of Haüy's principle (section 1 of Chap. I) enters here, however, the cubic system being obviously excluded from its operation as regards external interfacial angles. But the physical properties of the alums do, of course, vary,

each having its own optical, elastic, thermal, and electrical properties and constants.

The Work of Wollaston.—In the year 1809 the reflecting goniometer, for measuring the interfacial angles of crystals, the essential instrument of the crystallographer's laboratory, was invented by W. H. Wollaston, an event of far-reaching importance. As the result of the first careful angular measurements with it, the first goniometer or other instrument of sufficient accuracy constructed, he showed, in a memoir * published in 1812, that the orthorhombic carbonates of barium, strontium, and lead, namely, witherite BaCO_3 , strontianite SrCO_3 , and cerussite PbCO_3 , crystallised similarly, that also the orthorhombic sulphates of these same three metals, barytes BaSO_4 , celestite SrSO_4 , and anglesite PbSO_4 , formed similar crystals; and again, that likewise the rhombohedral carbonates of calcium, iron, and magnesium, namely, calcite CaCO_3 , siderite or chalybite FeCO_3 , and dolomite $\text{CaMg}(\text{CO}_3)_2$, formed crystals of very similar character. In this very important work he made it quite clear that the angles of the similar forms were not identical, but differed quite appreciably, well beyond the possible experimental error of his goniometer. Hence he never challenged Häüy's principle, for there was no occasion to do so. For instance, he gave for the rhombohedral angle of calcite $105^\circ 5'$, for that of dolomite $106^\circ 15'$, and that of chalybite $107^\circ 0'$, precisely the values accepted to-day after repeated remeasurement by several later crystallographers.

These measurements of Wollaston, exact and definite, did not, however, attract the attention they deserved, and appear to have been ignored on the Continent, although they were published in the well-known *Transactions* of our Royal Society. Indeed, Malus appears to have made similar measurements a few years later, with a good

* *Phil. Trans. Roy. Soc.*, 1812, 1, 160.

goniometer on Wollaston's principle, and to have obtained exactly the same angular values for the principal angles. Biot also published confirmatory evidence, and von Fuchs in 1815 called attention to the facts relating to the barytes group of sulphates.

There can be no question whatever that to Wollaston belongs the credit of having not only discovered isomorphism, but of showing that outside the cubic system isomorphous substances possess their own exact form, with angles distinct from those of every other substance, even those of the same isomorphous series. It is high time that this credit were assigned to him.

The Work of Mitscherlich.—In the year 1819 Eilhard Mitscherlich, a young student working at his first research in the university laboratory at Berlin, and apparently quite unaware of Wollaston's work, observed that the four acid phosphates and arsenates of potassium and ammonium, H_2KPO_4 , $\text{H}_2(\text{NH}_4)\text{PO}_4$, H_2KAsO_4 , and $\text{H}_2(\text{NH}_4)\text{AsO}_4$, crystallise in similar tetragonal prisms terminated by primary pyramid faces (only these two forms, the square sectioned prism and square pyramid at each end being present), and also that the four neutral di-potassium and di-ammonium salts of the same two acids, of the type HK_2PO_4 , likewise crystallise similarly to each other in monoclinic crystals. He at once studied sufficient crystallography under Gustav Rose, the Professor of Mineralogy, to enable him to establish these facts fully by goniometrical measurements. But the lack of a sufficiently accurate goniometer in the Berlin laboratory, and the difficulty of getting very good crystals, led him to consider that the similar crystalline forms were composed of faces inclined at identical angles.

This appeared to him completely to controvert Haüy's principle, that every substance has its own peculiar form and interfacial angles. Mitscherlich next observed the fact, published seven years previously by Wollaston, that

the mineral rhombohedral carbonates of the calcite group, calcite CaCO_3 , chalybite FeCO_3 , dialogite MnCO_3 , and dolomite $\text{CaMg}(\text{CO}_3)_2$, also crystallise in apparently identical forms; and then also that the orthorhombic sulphates of the barytes group, likewise fully studied by Wollaston, barytes BaSO_4 , celestite SrSO_4 , and anglesite PbSO_4 , do likewise.

These confirmations of Wollaston's work by Mitscherlich, without any reference to it by the latter, render the conclusion unavoidable that he was unaware of it. For if he had been cognisant of the fact brought out so clearly by Wollaston's exact measurements, that small but real differences occurred in the angles between the crystal faces, he would never, even at this time, in the first stage of his first research, have contested Haüy's principle, and assumed identity of form to occur in the cases of the members of each set of compounds. The controversy which now arose, in which Haüy himself strongly took part, rejecting Mitscherlich's conclusion with great emphasis, need never have commenced if Wollaston's work had been known, and the Continental scientists had taken proper note of published British work. The controversy had the good effect, however, of causing Mitscherlich to work hard at extending the scope of his researches, and he turned his attention to some readily-prepared artificial salts, obtainable in good crystals of which he could ensure the purity, namely, the sulphates of dyad-acting metals known as the "vitriols." They comprise Epsom salts, magnesium sulphate; white vitriol, zinc sulphate; green vitriol, ferrous iron sulphate; and blue vitriol, copper sulphate. He also included the corresponding pale pink sulphate of manganese, the red sulphate of cobalt, and the green sulphate of nickel in his investigation. These salts had previously been investigated by Beudant, but only qualitatively, so that he never discovered that the crystals contained water of crystallisation, and in different amounts, which rendered

his conclusions untrustworthy. He did show, however, that under certain circumstances mixed crystals of the different salts could be obtained; he observed that the addition, for instance, of fifteen per cent. of ferrous sulphate to zinc sulphate, or nine per cent. to copper sulphate, would cause zinc or copper sulphate to crystallise in the same form as ferrous sulphate, and quite differently from their usual forms. Mitscherlich went thoroughly into the matter, with pure salts and quantitative analyses at every step, and he eventually established the following facts. The Epsom salts group crystallises in the rhombic system, with seven molecules of water of crystallisation, and consists of magnesium sulphate itself $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, zinc sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and nickel sulphate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. A second group consists of the sulphates of ferrous iron and cobalt, and also has seven molecules of water, namely, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, but forms monoclinic crystals. A third group consists of copper and manganese sulphates, both crystallising in the triclinic system with five molecules of water of crystallisation, namely, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$. This is only true of manganese sulphate, however, when the temperature is between 7° and 20° ; for if lower than 7° rhombic crystals of $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$, like those of the Epsom salts group, separate, while if higher than 20° the crystals have only four molecules of water and are tetragonal.

Mitscherlich next observed another new fact, that if a crystal of a member of either of the first two heptahydrated groups be dropped into a saturated solution of the other, crystals will be deposited like the crystal introduced. Hence he concluded that both of the heptahydrated groups are capable of forming crystals of the two different forms, rhombic and monoclinic, and are what became termed "dimorphous." At ordinary temperatures the one group forms most readily the rhombic crystals, and the other group the monoclinic ones.

Later Mitscherlich established that carbonate of lime, CaCO_3 , is likewise dimorphous, the two forms being the well-known calcite, which is trigonal-rhombohedral, and aragonite, the much-discussed rhombic form. Again in 1823 he discovered that sulphur has a second, monoclinic, form, which he obtained by fusing the ordinary rhombic variety, allowing the "melt" to cool and partially to solidify, and pouring out the remaining liquid, when monoclinic needles were left behind, radiating from the walls of the vessel.

At the invitation of the celebrated Swedish chemist Berzelius, who visited Berlin in 1819, Mitscherlich went to work in the laboratory at Stockholm, and while there, at the suggestion of Berzelius, he gave the name "Isomorphism" to the phenomenon that analogous elements can replace each other in their crystallised compounds without any apparent change of crystalline form. He probably entertained at this time, 1819, the more rough and ready view of identical similarity. But later there can be no question that he modified his view so as to admit small differences of angle. This is shown by his order to the optician Pistor for the most accurate Wollaston goniometer that he could construct, and also by the following, his last, definition of isomorphism. "Substances possessing an analogous composition, which crystallise in the same form, or in similar forms, and which are capable of mixing in all proportions, are isomorphous."

The true sense in which this is correct, and the limitations required to the last part of the definition, will be made clear in subsequent chapters.

As leading up to the author's own researches, which had for their object the settling of this question, reference may be made to two further stages of Mitscherlich's researches. He completed his first year's work in 1819 by preparing for the first time the important and splendidly

crystallising double sulphates of potassium and dyad-acting metals, which crystallise in the monoclinic system with six molecules of water of crystallisation, by mixing a solution of potassium sulphate with a solution of any one of the sulphates of the "vitriol" groups which have been so considerably referred to. Again, in 1827 he made the first preparation of selenic acid, H_2SeO_4 , the selenium compound corresponding to sulphuric acid, the element selenium having been discovered by Berzelius. Of this selenic acid he prepared the potassium salt, and showed it to be rhombic, isomorphous with potassium sulphate. He also prepared selenates of the dyad-acting metals, and showed that they formed excellent monoclinic crystals of double selenates with potassium selenate, containing also six molecules of water of crystallisation, and completely analogous and isomorphous with the double sulphates. It is these splendidly crystallising salts, the simple rhombic sulphates and selenates of potassium and its alkali analogues, and the monoclinic hexahydrated double sulphates and selenates, which the author has employed as the subjects of a thirty years' research, recently completed. Moreover, it was Mitscherlich who showed that the chromates and manganates are isomorphous with the sulphates and selenates, and also that the perchlorates and permanganates are isomorphous with each other.

Historical Chemical Uses of the Principle of Isomorphism.
—Quite apart from the question of the strict interpretation of the term isomorphism, a result of immense importance to chemistry at once sprang from the magnificent work of Wollaston and Mitscherlich, largely owing to the fact that Berzelius, who was so interested in Mitscherlich, was the greatest living authority on the equivalents and atomic weights of the elements. It was obvious that the substances which were shown to be isomorphous were chemically analogous, and it was usually the case that an isomorphous group was formed by the interchange of

elements belonging to the same family group, or acting chemically similarly, that is, the different members of the isomorphous series were of similar chemical constitution, and only differed in having present in each case a different member of a family group of closely allied and similarly behaving chemical elements. Thus in the sulphate-selenate series, selenium, which is an element of the sulphur group, having similar combining power (valency) and forming the same type of compounds, replaces sulphur without immediately apparent change of crystal form. Now Berzelius, in studying the chemical relationships of all the elements known up to that time, had found great difficulty in fixing the atomic weights from the equivalents, and thereby defining their positions among the elements, of quite a number of elements, and not only indeed the rarer and more lately discovered ones. But here in the principle of isomorphism was a new ally, and most of these difficult cases were at once cleared up by the application of the new principle, the salts of these elements being found to be isomorphous with those of well-understood elements about whose positions there was no ambiguity. The elements which he thus correctly placed in position, and the atomic weights of which he was able to fix, were copper, cadmium, zinc, nickel, cobalt, iron, manganese, chromium, sulphur, selenium, and chlorine. Also the queer case of the ammonium salts, in which the base ammonium was known to replace potassium isomorphously, was eventually settled. For at this time the constitution and composition of ammonium was a matter of bitter controversy. It was finally shown that it was ammonia gas, nitrogen hydride, NH_3 , with an additional atom of hydrogen, namely, NH_4 , that acted as a radicle or group-entity in replacing an atom of potassium.

Two later cases of special interest were those of the rare and little-known elements tantalum and niobium, the atomic weights of which were investigated by Marignac

in 1864. They are characterised by forming yellow, fusible and volatile chlorides (now known to be pentachlorides). It was discovered that the compounds of these two metals were isomorphous; their pentoxides occur in isomorphous mixture in several minerals, and the double fluorides with potassium fluoride, KF , namely, K_2TaF_7 , and K_2NbF_7 , crystallise readily in similar forms. The law of Dulong and Petit, connecting atomic weight with specific heat, had not then been discovered, and the vapour density of tantalum chloride had been determined by Deville and Troost with impure material, so that the result was misleading and puzzling, as it did not point to a pentachloride. Marignac decided the question, however, from the isomorphism of their compounds, showing that the atomic weights of tantalum and niobium must respectively be 180 and 93. But it was not until considerable time had afterwards elapsed that he was fully believed, when Deville and Troost were able to make fresh determinations of vapour density with pure material, and found that Marignac was right, the formula of the chloride being TaCl_5 . Moreover, it has since been thoroughly well established that niobium and tantalum belong to the vanadium group of elements, occupying the positions in it which Marignac's atomic weights would give them. Niobium is now, however, more rightfully called columbium, the name given to it by its discoverer Hatchett in 1801, as it was found in a mineral from Massachusetts.

Gallium is another element the correct chemical position and atomic weight of which, from two possible alternatives, was settled by use of the principle of isomorphism. This interesting element was discovered by Lecoq de Boisbaudran in 1875 in zinc blende from the Pyrenees. It was found that its sulphate forms an alum with ammonium sulphate, so that gallium must be capable of replacing aluminium in the alums, and therefore its sulphate must be $\text{Ga}_2(\text{SO}_4)_3$, analogous to aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$.

This corresponded to the atomic weight 69.9, and quite excluded any other possible alternative. Again the conclusion was later fully confirmed by the eventual determination of the vapour density of the chloride, GaCl_3 , and as Dulong and Petit's law was now also known, by determinations of the specific heat of the pure metal.

Vanadium also was finally allocated to its correct position among the elements, and its atomic weight determined without ambiguity, from two alternatives accurately afforded by analyses of its salts, by Roscoe, from considerations of isomorphism. His first important discovery, made in 1867, was that the substance considered by Berzelius to be vanadium, and to which he attributed properties which classified it with chromium and molybdenum, was not the element itself, but the nitride, which is a metallic-looking scaly substance. For vanadium proved to possess the very uncommon property of combining directly with nitrogen. Eventually Roscoe isolated the pure element by reducing the dichloride in hydrogen gas, and found it to belong to the nitrogen-phosphorus-columbium group, a conclusion which appeared to be indicated from the first, by the isomorphism of its principal mineral and natural source vanadinite, lead chloro-vanadate $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$, with apatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, the lead replacing the calcium and vanadium the phosphorus of the latter. Further evidence was afforded by the fact that, in combination with oxygen, vanadium forms a vanadyl group VO which can replace the corresponding columbium radicle CbO in several compounds containing the radicle. Thus the evidence of isomorphism was overwhelming, and it was a great satisfaction when Roscoe isolated the real element itself and found the indications of isomorphism to be completely confirmed. Hence, vanadium was assigned to its proper and now well-established place in the nitrogen group, with an atomic weight of 51.

Definite Indications of Angular Differences in Isomorphous Crystals.—It has already been mentioned that, in the cases of the rhombohedral carbonates, Wollaston in 1812 had shown that there was a clear difference of one to two degrees in the rhombohedral (principal) angle of the different members of the group. The following table embodies his results, and completes them with later determinations for other members of the group.

Values of Rhombohedral Angle in Calcite Group.

Calcite, CaCO_3	74° 55'
Magnesite, MgCO_3	72° 36'
Chalybite, FeCO_3	73° 0'
Calamine, ZnCO_3	72° 20'
Rhodochrosite, MnCO_3	72° 58'
Dolomite, $\text{CaMg}(\text{CO}_3)_2$	73° 45'

It will be clear from the table that the maximum difference observed in the rhombohedral angle of this group of isomorphous minerals is $2\frac{1}{2}$ degrees. The interchangeable metals are not all, however, those of one and the same family group, so that no regular law is apparent, but only a clear difference.

Another more recent case of a clear difference, this time due to interchange of family group analogues only, is that of the red silver ores, the minerals proustite, the sulpharsenite of silver Ag_3AsS_3 , and pyrargyrite, the corresponding sulphantimonite of silver Ag_3SbS_3 , which were investigated by H. A. (now Sir Henry) Miers in 1887. Here the interchangeable elements, arsenic and antimony, belong to the same nitrogen-phosphorus group of the periodic table of the elements. The crystals of proustite possess a magnificent red (vermilion) colour, and afford a bright red "streak" on scratching. Pyrargyrite is dark grey, and gives a reddish-purple streak. Both are especially beautiful objects, which, however, have to be stored in the dark and can only occasionally be brought out for a few moments into daylight; for they are so sensitive to light, like many other of the compounds of

silver, that they are rapidly decomposed by bright sunlight. They crystallise in the ditrigonal polar class 20 of the trigonal system, the second order hexagonal prism being principally developed, terminated by the semi-forms of the primary rhombohedron, other rhombohedra, scalenohedra, and pyramids, the two ends being quite different, in accordance with polar class symmetry. A typical crystal of either mineral is represented in Fig. 20. The rhombohedral angle of proustite was found to be $72^{\circ} 12'$, and that of pyrrargyrite $71^{\circ} 22'$, the angular difference being thus nearly a degree, $50'$. The other

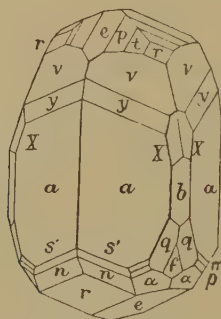


FIG. 20.—Crystal of Red Silver Ore.

angles also showed clearly measurable differences in the cases of the two substances.

There can be no doubt that Mitscherlich, in his maturer years, came to admit the wider interpretation of isomorphism which permits of these slight angular differences between the members of an isomorphous series. It is to be regretted that he never used the excellent goniometer made by Pistor for him, as already mentioned, to make further measurements with the higher accuracy which it rendered possible; instead, he carried out a research on the effect of rise of temperature on the interfacial angles of crystals.

Besides similarity of chemical constitution and behaviour,

due to the interchangeable elements forming the isomorphous series being members of the same family group, equality in the number of atoms present in the members of a series was at first also supposed by Mitscherlich to be a condition of isomorphism, but his own example of the isomorphous replacement of potassium by the ammonium radicle NH_4 obviously ruled out this idea later. It would, of course, admit cases like sodium nitrate and calcite, NaNO_3 and CaCO_3 (see page 141), both of which are rhombohedral, and having like structural constants will grow together. This case will be dealt with more fully later.

Another condition which he specifies even in his later definition of isomorphism, the capability of forming mixed crystals in all proportions, is only partially true, as the two extreme end members of a series will be shown later to be often incapable of admixture, their structural constants and dimensions being too far apart for congruency.

Since the time of Mitscherlich many new series of isomorphous substances have been prepared and described, but no further progress was made up to the year 1893, beyond that derived from the research on the red silver minerals just described. The accumulated data were considerable, but chaotic and quite unconnected, and, as will be shown at the beginning of the next chapter, not infrequently totally incorrect and misleading.

CHAPTER III

IMPROVED METHODS OF CRYSTALLOGRAPHIC RESEARCH

IN the year 1893 the author published the first of a long series of papers giving the results of a research, extending over thirty-two years to the present year 1925, on "The Relations between Crystalline Structure and Chemical Constitution." In the commencement of that first memoir the following occurs, which will throw light on the situation at that time.

"The direction in which pure crystallographic research appears likely to afford results of the greatest interest and significance is that in which comparable measurements are made upon crystals of substances chemically related to each other in a definitely ascertained manner. The information at present (1893) available, particularly with regard to the goniometrical effect produced by the replacement of one metal in an isomorphous series of salts by another, is of the most meagre and insufficient character. The absence of conclusive data is, however, largely to be accounted for by the fact that, especially in the cases of substances crystallising in the higher systems of symmetry, the values of analogous angles upon the crystals of the various members of the series are so nearly identical that the differences frequently fall within the limits of the few minutes usually assigned to experimental and formational error."

The author had selected two series of splendidly crystallising salts for a systematic attack, both of which have been referred to in the last chapter in describing the work of Mitscherlich, namely, (1) the rhombic sulphates and

selenates of the alkalies, $R_2S[Se]O_4$, where R is not only potassium or ammonium, the salts known to Mitscherlich, who prepared the selenates for the first time, but also the rare metals rubidium and caesium, discovered by Bunsen in 1861 and 1860 respectively, and which belong to the alkali-metal group and in many ways resemble potassium, and also the rare metal thallium, which was discovered by Sir William Crookes in the same year as rubidium, 1861, and which in its thalious capacity is capable of replacing potassium, isomorphously; and (2) the double sulphates and selenates of the monoclinic series crystallising with six molecules of water of crystallisation, $R_2M(S[Se]O_4)_2 \cdot 6H_2O$, in which the salts just referred to under (1) are respectively combined with one of the sulphates or selenates of dyad-acting metals, M representing magnesium, zinc, iron, manganese, nickel, cobalt, copper, or cadmium. Ten salts, the complete set, of series (1) have been very fully studied, and 64 salts of series (2), the series which was entirely discovered and first prepared by Mitscherlich, as regards their potassium and ammonium members, with which, of course, he was alone acquainted, rubidium, caesium, and thallium not having then been discovered.

When we compare the crystal-axial ratios for the alkali sulphates which were current in 1893, namely, those for potassium sulphate as measured in 1830 by Mitscherlich, those given by Bunsen in 1861 for rubidium sulphate, and those determined by von Lang in 1867 for caesium sulphate, we find them, as shown in the accompanying table, to bear no relation whatever to the atomic weights of the interchangeable alkali metals:—

For K_2SO_4 ,	$a : b : c = 0.5727 : 1 : 0.7464$
„ Rb_2SO_4 ,	$a : b : c = 0.5723 : 1 : 0.7522$
„ Cs_2SO_4 ,	$a : b : c = 0.5805 : 1 : 0.7400.$

This order, however, proved to be incorrect, for the result derived from a large number of measurements of

the interfacial angles from which these ratios have to be calculated, made with especially perfect crystals, prepared with very great care, was as follows:—

For K_2SO_4 , $a : b : c = 0.5727 : 1 : 0.7418$

„ Rb_2SO_4 , $a : b : c = 0.5723 : 1 : 0.7485$

„ Cs_2SO_4 , $a : b : c = 0.5712 : 1 : 0.7531$.

The correct order is thus seen to be that of the three elements, potassium, rubidium, and caesium, in the first group of the periodic table of the elements, and of their atomic weights and atomic sequence numbers (atomic numbers). Hence, it was obvious how necessary a reinvestigation had become.

The whole research, which began in 1890, has involved the measurement of over 45,000 crystal angles, the carrying out of over 500 density determinations, and the preparation of more than 2000 truly plane-faced section-plates, rectangular blocks, and 60° -prisms, out of the small and relatively soft crystals of these artificial salts, with which optical, thermal, and other physical measurements have been made, the optical observations being carried out for light of all parts of the spectrum the wave-lengths of which were accurately known.

It was at once found that the experimental means then available were totally inadequate, for every purpose except that of crystal-angle or refractive index measurement. For the measurement of crystal angles the No. 2A Fuess horizontal-circle goniometer* (reading to half-minutes) was, and remains unbeaten for convenience and accuracy; and the No. 1A Fuess larger instrument,* reading to seconds, is the most efficient instrument for refractive index measurement by the best of all methods, that of the 60° -prism when cut to afford two of the three indices of these rhombic and monoclinic salts directly, one afforded by light vibrating parallel to the refracting edge and therefore to one of

* Described and illustrated in "Crystallography and Practical Crystal Measurement," 2nd ed., Vol. I., pp. 36 and 436, and Vol. II., p. 1040.

the three axes of the optical ellipsoid, and the other corresponding to vibrations perpendicular to the edge and parallel to a second of the principal axes of the ellipsoid. Also the Fuess larger polariscopical suspended goniometer,* having a circle like that of the No. 2A goniometer, is excellent for the measurement of optic axial angles by use of the interference figures in convergent polarised light, afforded by section-plates perpendicular to the acute and obtuse bisectrices.

But before the two excellent instruments * last mentioned could be used it was obviously imperative to obtain the essential 60° -prisms and section-plates out of the crystals, true to the proper orientations with respect to the crystal faces, with which to make the determinations of refractive index and optic axial angle; and also section-plates for extinction determinations (fixing the position of the optical ellipsoid) in parallel polarised light. Now no apparatus was available for preparing these plates and prisms, with truly plane surfaces exactly orientated with respect to the crystal symmetry. Hence the author caused an instrument to be constructed by Messrs. Troughton and Simms for the purpose, the "Cutting and Grinding Goniometer," which enables surfaces to be prepared which are both truly plane and correctly orientated to within two minutes of arc, either by cutting (if the crystal be hard, a natural mineral crystal, for instance), or grinding (necessary for all crystals, either after cutting or straightaway if relatively soft, such as the crystals of laboratory preparations, salts, etc.), the ground surface being eventually also polished on the instrument, so as to retain the true plane-ness. The perfected instrument now in constant use in the author's laboratory, and which has been so since its completion in the year 1898, being still as efficient as ever, was the third which was constructed, the first, constructed in 1894, having been for grinding and polishing

* See footnote on p. 50.

only, for use with artificial salts and other laboratory preparations or natural very soft crystals. The second was for cutting also, and is in the Science Museum at South Kensington. The third, already referred to as in the author's laboratory (the first being also there), has a few final improvements, but is essentially like the second. It is shown in Fig. 21. Without this instrument the research would have been impossible, and although the cost was naturally very high, it is amply repaid by the efficient work done.

The reason why published optical crystallographic data are so scarce, and confined almost entirely to hard mineral crystals, is that no efficient means of preparing surfaces required on soft crystals have hitherto been available. Prof. F. E. Wright has recently described one in America which is practically on the lines of the author's instrument, but not so convenient. Less ambitious but useful pieces of apparatus, in many parts, for grinding surfaces on crystals, have also been devised by Wülfing and by Thomas, the last-mentioned being much the more efficient, although, of course, not nearly so convenient or accurate as the author's Cutting and Grinding Goniometer.

The Cutting and Grinding Goniometer.—A few words of description may perhaps be usefully given of this invaluable instrument, the third model of 1898, shown in Fig. 21.

It is essentially a suspended goniometer, with a very accurately divided horizontal circle, and the usual telescope and collimator, and crystal-attaching and -adjusting apparatus, as for the best goniometers, but with the two adjusting segments divided on silver arcs with indicators. In addition, there are provided the following parts:—

(a) The crystal-cutting gear is composed of a soft iron cutting disc fed on its edge with diamond powder, which has been pressed into it by an agate held against it while rotating, and suitable hand- and motor-driving pulley gear; the whole is carried by an arm which rotates about the back

column of the instrument, and the front end of which locks into a guiding gear attached (removable when not

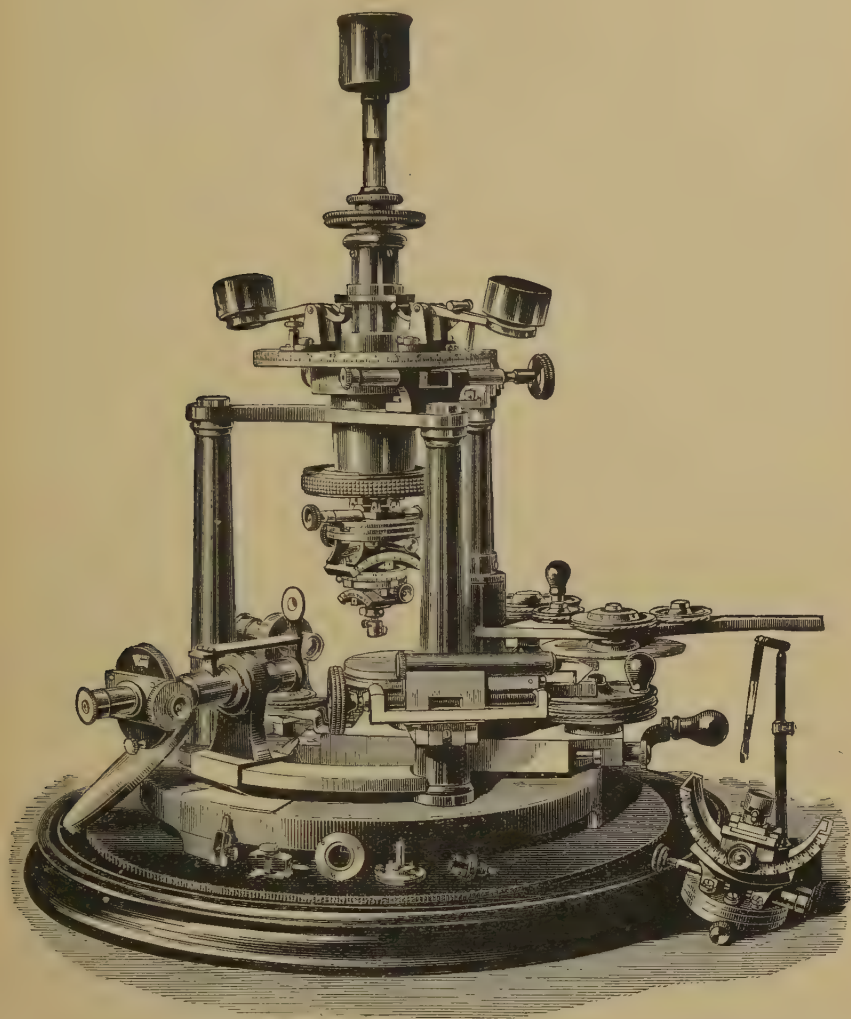


FIG. 21.—The Cutting and Grinding Goniometer.

needed) to the front pillar, and the milled head of which enables the operator to traverse the cutter through the crystal with the left hand, while rotating the cutter with

the right hand. A safety back-spring is provided to prevent jamming or the breaking off of the crystal end.

(b) The grinding and polishing lap and its rotating gear form a separate fitting, for hand- (usually preferable in this very delicate work with soft crystals) or motor-driving. The whole is mounted on a slider working in a dove-tailed bed passing through the centre of the basal table of the instrument, to enable the grinding part to be varied and prevent grooving. A dozen laps of different materials are provided, interchangeable in a moment, by means of a simple fitting and locking device carried by the circular rotating table, which actually carries the lap chosen for use. For these artificial salt crystals ground glass laps of two stages of fineness of grinding are used for the rough and fine grinding of the desired surface, and a plate-glass lap for polishing. For hard mineral crystals and their polishing, laps of bronze, cast-iron, steel, hard white-metal, pewter, boxwood (for use with putty powder), emery, opticians' wax, and felt are provided.

(c) A special axis is provided, between the inner axis carrying the adjusting movements and crystal and the outer one carrying the divided circle, which is entirely designed for modifying the pressure of the crystal on the grinding lap, and so to safeguard against fracture of the relatively soft crystal. It is made capable only of vertical motion, and is counterbalanced by two lever arms carrying weights. The most effective way of using it is to throw one lever, preferably the right-hand one, out of gear, leaving half the weight of the axis effective, and to manipulate the left counterpoise with the left hand, which enables the pressure to be varied to a nicety, from nothing up to half the weight of the axis and whatever it carries. This device has rendered breakages of crystals of very rare occurrence.

(d) Besides the ordinary adjusting and centring movements, there is an alternative set provided, shown on the

right of the plinth, on the table, which enables a 60° -prism to be ground with one setting of the crystal on the crystal-holder, which always occurs with opticians' wax, a variety which sets almost at once after warming to use. This alternative gear has an extra cylindrical movement of twice the usual size, enabling a movement of about 70° on each side of the vertical plane to be made, after the adjustment has been carried out with the ordinary two cylindrical movements. For when the adjustment has been made, of the plane within the crystal which is to be the bisecting plane of the 60° -prism, perpendicular to the grinding plane, the desired refracting edge of the prism being arranged also in the adjustment to be parallel to the grinding plane and to the axis of the large divided segment, it will be obvious that, starting with this latter at its 0° central position, if one rotates it for 60° on one side, and then grinds a surface, and then rotates it back to the central position and again further to the 60° graduation on the other side, and again grinds a surface, one will have produced an accurate 60° prism, with refracting edge and bisecting plane orientated as desired.

(e) Only one further device need be mentioned, among many other conveniences provided. It is one to enable the second parallel surface of a section-plate to be ground without the trouble of a separate adjustment. When the first surface has been ground and polished in the usual way, after a careful use of the goniometrical means of adjustment to the desired orientation, the crystal is cemented, by hard Canada balsam dissolved in benzene, to a little circular disc of truly parallel glass. This fits into a little cap with central hole large enough for the crystal to project clearly through it. The cap is then fitted over a special crystal holder in the form of a true-plane, a very thick (for rigidity) circular disc an inch in diameter with central stem for attachment in the holder-socket at the bottom of the inner axis of the instrument. This true-plane automatic-

ally becomes parallel to the grinding lap when placed in position with all adjusting movements at their zero position. The glass plate is tightly pressed against the truly-plane surface, when the cap is in position, fixed to the plane by little side screws, and as also the glass plate has parallel surfaces the first ground surface of the crystal must also be truly parallel to the grinding plane, and the crystal projecting out from beneath the cap can be ground down as much as is desired, thus making a surface parallel to the first and giving the required thickness or thinness to the section-plate. For the annular rabbett which holds the plate is so far countersunk that the cap is left very thin here, at the edge of the hole, enabling very thin sections to be ground if necessary.

So much has been said of this instrument because it is really the essential one of the research, and the author owes everything to it. After nearly thirty years' work it is as perfect and true as ever.

Apparatus for Providing Monochromatic Light.—As the research developed it was found necessary to devise a spectroscopic monochromatic illuminator to furnish a strong light of any desired wave-length at a moment's notice, in order that the optical constants could be determined for the desirable series of wave-lengths. This instrument is shown in Fig. 22. It enables only the three-hundredth part of the spectrum to be used, while affording brilliant illumination of the signal-slit images when refractive indices are being determined, the electric arc being the source of light. It also gives a very bright field of interference figures in the convergent-light polariscope, when measuring optic axial angles, and enables the exact wave-length to be determined for production of the apparently uniaxial cross and rings in cases of crossed axial-plane dispersion (to be illustrated later). It consists of a spectroscope with large objectives and a specially large prism, in order to pass as much light as possible while keeping the

slit fine and preserving spectroscopic purity of the eventual monochromatic light. The prism is interesting. Its truly plane faces are $4\frac{1}{2}$ by $2\frac{1}{2}$ inches, and it is quite colourless while having exceptionally large dispersion, nearly twice that of ordinary flint glass. It was made from half of a special block of glass made by Messrs. Chance for the late Sir William Huggins, who used the other half for the prism of his star spectroscope. It is curious that efforts to repro-

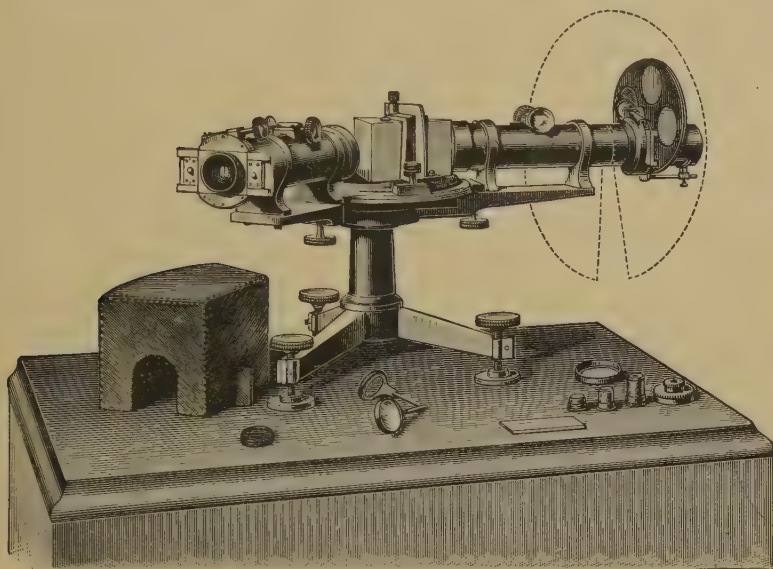


FIG. 22.—Spectroscopic Monochromatic Illuminator.

duce this glass have ever since failed, for the product has never had quite so large a dispersion without absorptive colour. It is thus a unique prism for the author's purpose. Moreover, it permits, when it is rotated for about seven degrees, of the whole spectrum being caused to pass the exit slit which, when the instrument is in use as illuminator, replaces the eyepiece; this occurs, too, while very nearly at minimum deviation, by rotation of the prism-circle which carries the prism rigidly attached to it. The circle graduations thus enable its position for the passage of light

corresponding to each of a large number of wave-lengths to be recorded in a table, and graphically represented in a curve, so that at any moment light of any particular desired wave-length can be made, by proper setting of the circle, to stream from the exit slit. In front of the latter (that is, outside it) is a ground glass diffusing screen, which just adequately diffuses the slit of light issuing from the exit slit to fill the whole field of the spectrometer (the large No. 1A Fuess instrument already referred to), or that of the polariscopical goniometer, with the monochromatic light. This instrument has also been of the greatest service, and is very satisfactory in its performance.

Messrs. Hilger now make a monochromator on the author's principle and with his collaboration, in which the prism is of the constant 90° -deviation type. Although the dispersion is not so great, this instrument also serves the purpose admirably, and can be fitted with the calibration drum provided with the Hilger spectroscopes.

The Necessity for the Refined Interferometric Method.—It was later found necessary to introduce the method of measuring in wave-lengths of light, by means of interference bands or fringes, Nature's own scale, black lines corresponding to half-wave-lengths on a ground of monochromatically coloured light of the wave-length chosen. The principle was first employed by Fizeau for the determination of the thermal expansion of crystals and other small bodies. For the amount of dilatation which so small a body undergoes is too minute for any ordinary mechanical method of measurement, the limit of which is the fifty-thousandth of an inch or two-thousandth of a millimetre. Now the scale of parallel rectilinear interference bands, produced by causing two rays of strictly monochromatic light (corresponding to a single unresolvable line of the spectrum) to interfere, enables a limit of measurement of the eight-millionth of an inch or the three-hundred-thousandth of a millimetre to be attained. For the clearly

defined black bands themselves mark half-wave-lengths, the eighty-thousandth of an inch when red hydrogen or red cadmium light (the latter quite unresolvable) is being employed, and the intervals, which can be made as wide as an apparent half inch, can be sub-divided by the eye into ten parts, and into a hundred parts by the micrometer carried by the eyepiece of the observing telescope.

There are two methods of working with interference bands or fringes, and these two terms, bands and fringes, characterise them. Fizeau worked with fringes (curved bands, usually parts of circles), and the author's improvement, besides the instrumental one, consisted in using rectilinear bands, for obviously they alone can be used with a micrometer carrying spider lines.

The two principles governing Fizeau's method and the author's are briefly as follows. (1) When the two reflecting surfaces which act as light sources are strictly parallel, the light monochromatic, and the thickness of the air film between the two surfaces not too great (within two millimetres for red C or greenish-blue F hydrogen light but up to a centimetre or two for red cadmium or yellow neon light, these two being unresolvable spectrum lines), and the telescope is adjusted for parallel rays (to infinity) and directed normally at the surfaces, a system of concentric circular interference fringes is seen, on looking through the telescope, around the centre of the field. When the thickness of the air film is increased, by the retrogression of one of the plates, the rings appear to move outwards, new ones appearing successively at the centre and progressively following the others outwards, getting closer together as they approach the edge of the field. If the air-film is made thinner the rings diminish and proceed towards the centre, where they disappear in turn. Both Michelson, and Fabry and Perot, have since used this principle in their researches. (2) If instead of being truly parallel to each other the two surfaces are minutely inclined so as to make

the air-film slightly wedge-shaped instead of equally thick throughout, the light being again strictly monochromatic and incident normally on the air-film in strictly parallel rays (under principle (1) the rays need not be parallel), and with the telescope focussed on the reference mark (a minute silver ring is most convenient) on one of the surfaces instead of being adjusted for parallel rays, then parallel rectilinear and practically equidistant interference bands are seen, parallel to the edge of the air-wedge between the two surfaces. This is the principle which has been employed by the author, being alone suitable for micrometric measurement and allocation. It was used by Pulfrich and since by Fabry and Perot in their well-known researches.

Fizeau used the upper plane surface of his crystal as one of the two surfaces, the lower one, and the under plane surface of a plano-convex lens as his second, upper, surface. The other surface of his crystal was matt, and so did not reflect, and the upper surface of the lens being curved did not reflect anything to interfere. But it caused him to obtain fringes and not rectilinear bands in any case, whether he used principle (1) or (2), and they were not suitable for micrometric observation. The author uses a glass plate and not a lens, and the second surface of the plate is inclined half a degree to the other instead of being strictly parallel, so that its reflection is side-tracked out of the way. To correct for a little dispersion thereby introduced, a second similar (duplicate) wedge-plate is used, so arranged as to correct the dispersion and also so that both its reflections are side-tracked. It is thus easy to isolate the two reflections which are alone wanted, and to make them interfere to the desired extent to produce a suitable field of bands.

The instruments devised for the application of this interferometric method were (1) a "dilatometer" for the measurement of the thermal expansion of crystals, using rectangular blocks of the crystals prepared on the cutting

and grinding goniometer; (2) an "elasmometer" for determining the modulus of elasticity by the bending of small crystal bars; (3) a "torsometer" for determining also interferentially the torsion coefficients of crystals; (4) a thickness-measurer for measuring the dimensions of the blocks, plates, bars, and rods of the crystals; and (5) an interferometer of general application, for measuring minute amounts of motion, such as that produced on the torsometer (its first application), or piezo-electric or other effects with crystals, or any short distances or changes in length or volume whatsoever.

The Interference Dilatometer.—In the original method of Fizeau, whose apparatus is preserved at the Bureau International des Poids et Mesures at Sèvres, where the author has had the privilege of seeing it, the instrument consisted essentially of a small tripod of platinum, like that shown in Fig. 24, on the thick central table of which the crystal rested, and on the three vertical screws of which, forming the tripod legs and passing through the table, was placed the lens, resting on the pointed tips of the screws by its plane face. The screws were so adjusted by screwing through the table that a thin film of air was left between the upper polished crystal surface and the under surface of the lens when the screws were firmly clamped to the table by little side screws. The whole was enclosed in an air- or oil-bath and the interference fringes were generated by directing sodium light at the surfaces and observing by a distant telescope. As each band passed a reference mark it was counted, and the number of bands, multiplied by half the wave-length of the sodium light employed, gave the alteration in thickness of the air-film during the process of the rise of temperature. What was afforded was the difference of expansion of the platinum screws (platinum being chosen for its small expansion as well as unalterability) and that of the crystal along the direction perpendicular to the surfaces and the table.

It will be observed that the light has to pass through the air-film twice, on going to the crystal surface and on returning reflected. Hence the interference bands, caused by the reflections from the two plane surfaces being allowed to interfere, correspond to half-wave-lengths of alteration of thickness of the air-film, the two journeys together making up a whole wave-length of retardation or difference of path between the two rays derived from the two respective surfaces.

The use of sodium light suited Fizeau's purpose fairly well. But the light is notoriously derived from two different yellow lines, D_1 of wave-length 0.0005896 and D_2 of wave-length 0.0005890 mm. The light from these two sources consequently periodically suffers self-interference, the bands periodically disappearing and reappearing. Sodium light is consequently not an ideal radiation for the purpose. Also, the Fizeau method, as already mentioned, using curved fringes, does not lend itself to micrometric measurement, nor does it fulfil another desirable condition, namely, normal incidence and reflection of the light on and from the reflecting surfaces. Benoit later used Fizeau's apparatus, in further work at the International Bureau, of which he was Directeur, but he used the alloy of platinum with ten per cent. of iridium, which is harder than platinum and more suitable, for the tripod.

The main defects of Fizeau's method were removed in a dilatometer of Abbe and Pulfrich, but owing to expense of platinum-iridium a steel or quartz tripod was used, and the form of apparatus adopted was again inconvenient, as the telescope was above the heated chamber. This defect has been remedied in the author's apparatus, and the tripod is like that of Benoit, of platinum-iridium, and weighs six ounces.

This dilatometer, which embodies the best features of all previous forms, together with several new ones, is shown in Fig. 23.

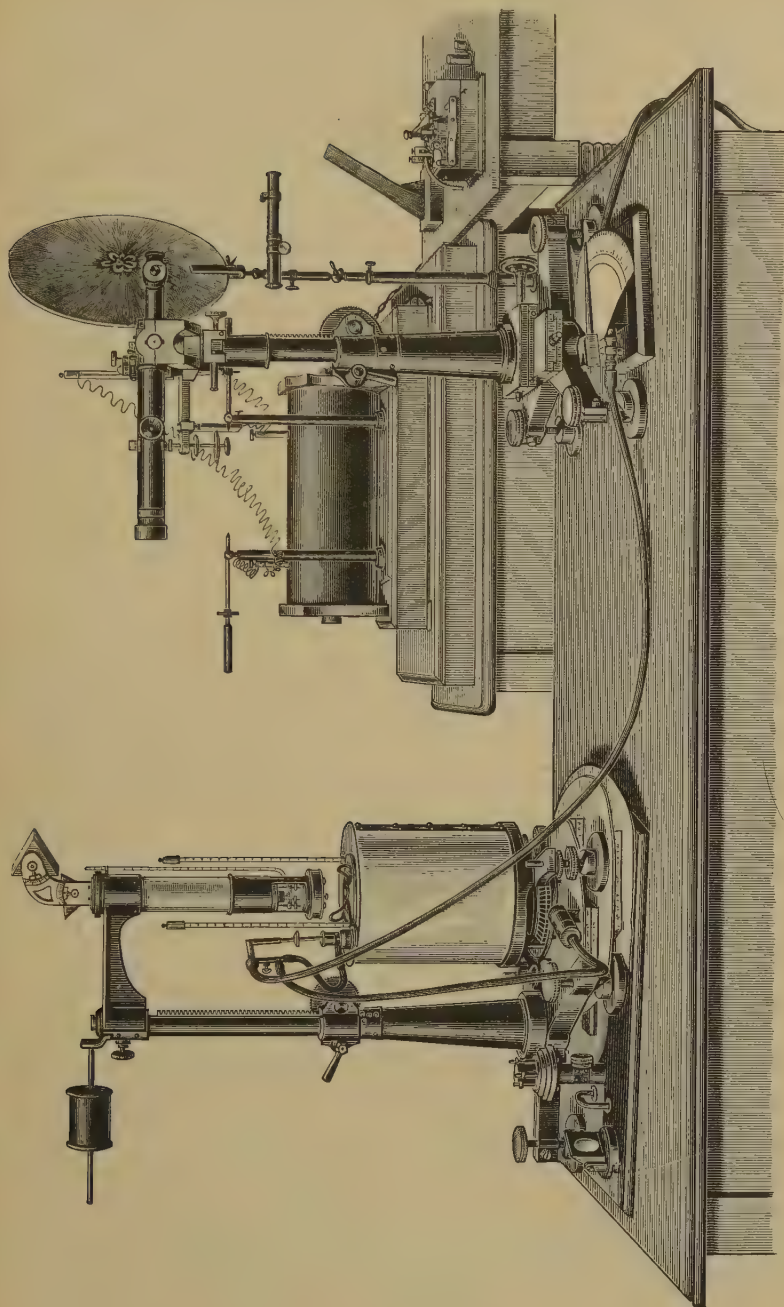


FIG. 23.—The Interference Dilatometer.

It is in two distinct parts, which are widely separated during the determinations of expansion, the interference apparatus and its heating chamber being on the left, and the observing apparatus on the right.

The source of light is a hydrogen or neon **H**-shaped Geissler tube, the end-on capillary forming a brilliant point-source of light at the end of the side collimator-tube of the auto-collimation telescope. At the crossing point of telescope and its side tube (common focus of both and of the eyepiece) is a little totally reflecting prism, which only half covers the aperture; a little rectangular stop (window) in the face of the prism nearest the objective actually serves as the immediate source of light, and the vertical long edge of this stop nearest the axis of the telescope is placed almost at the axis, as close as can be got to the open half of the aperture. The light then goes to the objective, the stop being at the focus of the latter, and thence across the intervening space as parallel rays, to the pair of dispersing prisms of the dilatometer part on the left. These are arranged so that the desired radiation, the red or green light of hydrogen or the neon yellow rays, is directed down the partially porcelain dilatometer tube to the interference apparatus at its lower end, where the platinum-iridium tripod, with the crystal in position on it, and the glass plate lying on its screws, are contained in a little chamber fitted with non-conducting base for its reception. The reflected rays then return by the same path almost exactly, the minute difference just being to let them through the open half of the aperture at the telescope common focus of objective and eyepiece, so as to be observed through the latter. When a determination is in progress, the dilatometer is lowered into the double air-path, and the temperature taken as the correct one is given by a thermometer with bent bulb-end strapped with silk to the tripod itself. All radiations, other than the two reflections which produce the bands, are screened off by an

iris diaphragm at the common focus, those, for instance, from the two surfaces of the countervailing wedge, which is carried in the roof of the little interference chamber just above the tripod and its glass disc.

Observations were usually made for two intervals of temperature, from the ordinary to about 65° , and from thence to about 120° C. This enabled not only the coefficient of expansion to be determined but also the increment of the expansion per degree. If α represents the coefficient of thermal expansion, the actual coefficient at any temperature t , and also the mean coefficient between any two temperatures whose mean is t , is then $\alpha = a + 2bt$. The mean coefficient of expansion between 0° and t° is, however, $a + bt$. These constants, a and b , can readily be calculated from the observations of the positions of the bands at the three limiting temperatures, and the number of counted bands passing the reference mark during the two intervals, this mark being a little silver ring on the glass surface resting on the tripod, and which is actually focussed by the telescope. The micrometer eyepiece is a special one, which not only focusses the spider lines (two parallel ones within which a band can be adjusted, and a horizontal one) of the micrometer, but also the silver ring and the interference bands themselves, which are localised in the air-film. The micrometer eyepiece is removed and replaced by a common eyepiece when reviewing the images of the little signal-stop source of light, for adjusting and screening-off purposes. The micrometer eyepiece has an additional lens, besides its positive ocular, which converts the whole telescope into one focussing the reference mark and bands.

With this dilatometer the coefficients of thermal expansion of the sulphates of potassium, rubidium, and caesium were determined for all three axial directions. Each determination for two intervals takes a minimum of five hours up to a maximum of seven hours, the whole process of the

movement of the bands being watched throughout as the only satisfactory way of being sure that the heating has gone steadily forward without any cracking of the crystal, which would probably entirely upset the adjustment of the bands. As the expansion along each axis was determined from six to eight independent times on different days, sixty-four determinations in all were made for these three salts, with very satisfactory results, which will be dealt with in a subsequent chapter. Also the expansion of the platinum-iridium of the tripod was determined, as this is naturally required in the calculations.

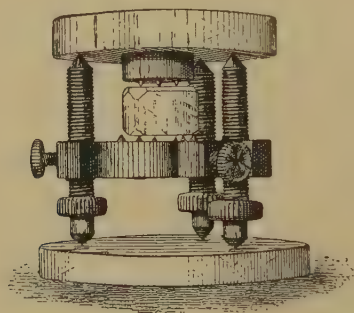


FIG. 24.—The Interference Tripod and Contents.

An additional determination of expansion was that of aluminium; for a small disc of aluminium was laid with three-point contact, over the crystal, to furnish the lower reflecting surface of the air-film, the crystals of these salts not taking a good enough polish themselves. Moreover, not only is the reflecting power of aluminium just about right to be of like intensity to the reflection from the glass surface in contact with the screws, but it expands 2.6 times as much as platinum-iridium, and so approximately compensates for the expansion of the screws, and thus practically the whole expansion of the crystal is shown directly in the interference band results. No attempt at exact compensation is, of course, made, and the expansion of

both the platinum-iridium and the aluminium were determined many times over with the greatest care, and the precise mean values for each were used in the calculations. The arrangement with crystal and disc on the tripod is shown in Fig. 24. The table of the tripod has three sets of three raised points of different heights to accommodate the crystal also with three-point (the only stable) contact.

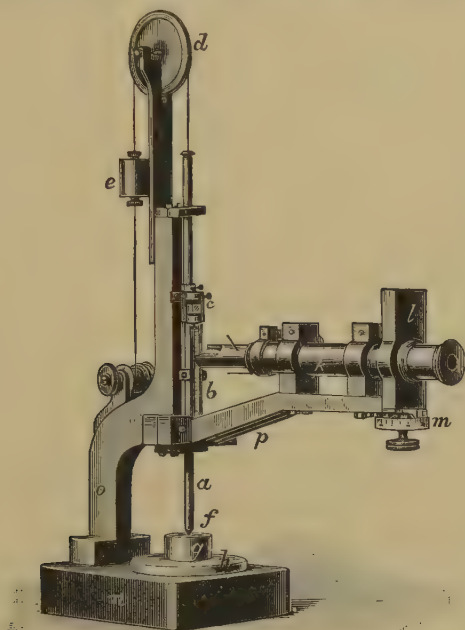


FIG. 25.—The Thickness Measurer.

The Thickness Measurer.—This is shown in Fig. 25. It is merely a vertical rod with a silver millimetre scale divided directly into fifths of a millimetre and suspended from gimbals in a nearly counterpoised manner; it is read by a telescope with micrometer eyepiece, which enables readings to be made to a thousandth of a millimetre.

The rectangular crystal-block or other object to be measured is laid on a thick glass base-plate, the centre of which is immediately under the rod, which terminates in

a rounded agate point. The rod is lowered on to the surface of the object by means of a little winch at the back of the curved columnar support. The base-plate rests with three-point contact on a basal gun-metal plinth, which is circularly recessed to take the glass disc without any possible side movement. After the conclusion of the expansion determination with the dilatometer, the platinum-iridium tripod and its contents are carefully transferred to the glass base-plate, adjusted centrally with respect to the latter, and the rod is lowered gently on to the top of the aluminium disc and a reading taken; the disc is then removed and the rod lowered on to the crystal and another reading taken; the crystal is then in turn removed, and the rod lowered on to the table of the tripod and a third reading taken. From these readings, and a knowledge, previously acquired once for all, of the height of the plane of the three points and of the plane of the tops of the platinum-iridium screws, it will be obvious that the lengths of the screws taking part in the expansion, and the thicknesses of the crystal and aluminium disc, can at once be derived.

Some typical results with the instrument will be given in a later chapter.

The Elasmometer.—The determination of the elastic bending of plates and bars of crystals was carried out by use of the same principle of half-wave-length interference band observation, the same autocollimation telescope on its separate pedestal, and dispersion and interference apparatus on its second pedestal, being employed as with the dilatometer. The only difference is that for the purpose of the elasticity work the little interference chamber carrying the platinum-iridium tripod is now detached from the lower end of the partly porcelain tube, and replaced by a simple cap with central aperture carrying in an annular rabbett the countervailing glass wedge-disc, one inch in diameter. The interference tripod is carried on this instrument on two gun-metal blocks, two screws on one

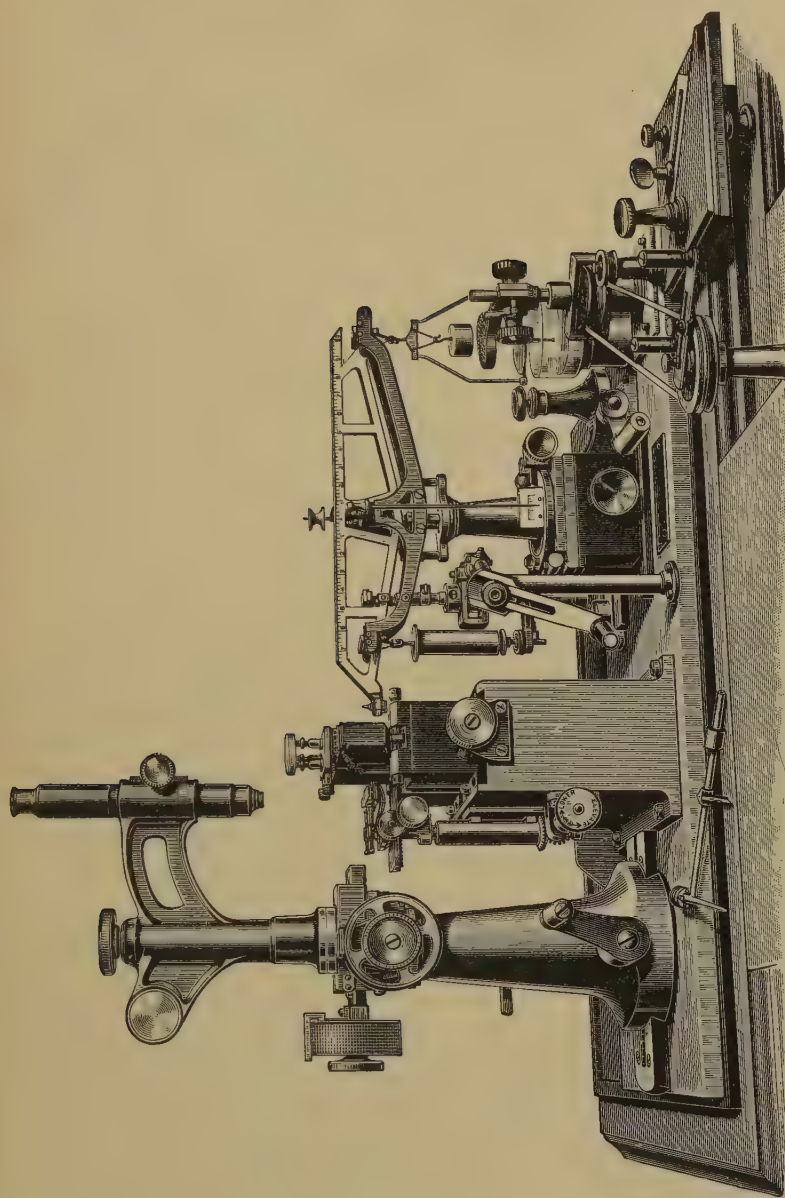


FIG. 26.—The Elasmometer.

block and one on the other, each of which carries underneath it a wedge of platinum-iridium, edge downwards and horizontal, up against which the bar of crystal is to be pressed, one wedge near each end, by the agate point carried at the end of a balance beam. It is through this point, exactly under the centre of the bar, that the pressure (bending weight) is delivered which is to bend the bar upwards at its centre, and which corresponds to the weight carried on the pan at the other end of the balance. All adjustments necessary are provided, for the exact parallelism of the wedge-edges and their convenient distance apart, for the exact placing of the pressure point of the balance to the bar centre, and for that of the bar itself, the nature of which adjustments will be more or less clear from the illustration, Fig. 26. The upward movement at the centre of the bar, when the weight is brought into operation by the release of the balance, is transmitted by a vertical delicately sliding rod of aluminium, carrying at its upper end a circular disc of thick black glass, mounted on a miniature adjusting table. The polished upper surface of this black-glass-head forms the lower of the two essential reflecting surfaces which are to produce the interference bands. The upper of these two surfaces is the same as for the dilatometer, the lower surface of the large colourless glass wedge-disc which carries the miniature silver ring as reference mark for the passage of the bands. This glass wedge-disc is, of course, laid on the tops of the tripod adjusting screws, in such an adjusted manner as to leave the usual millimetre-thick air-film between the black and colourless glasses. The arrangement of these essential parts will probably be best understood from the drawing in Fig. 27.

There is one further very essential provision on this apparatus, namely, for the control of the application of the load and a device for preventing flickering of the bands during its application. It will be obvious that if the load were applied by the simple release of the balance, as when

weighing, the whole of the interference bands corresponding to the amount of motion upwards of the bar centre, would rush by in a flash, without any possibility of counting them. So a delicate apparatus, including a coarse and a very fine movement, is provided at the right end of the balance where the weight is laid, to support the platinised weight until the right moment, and then to lower it

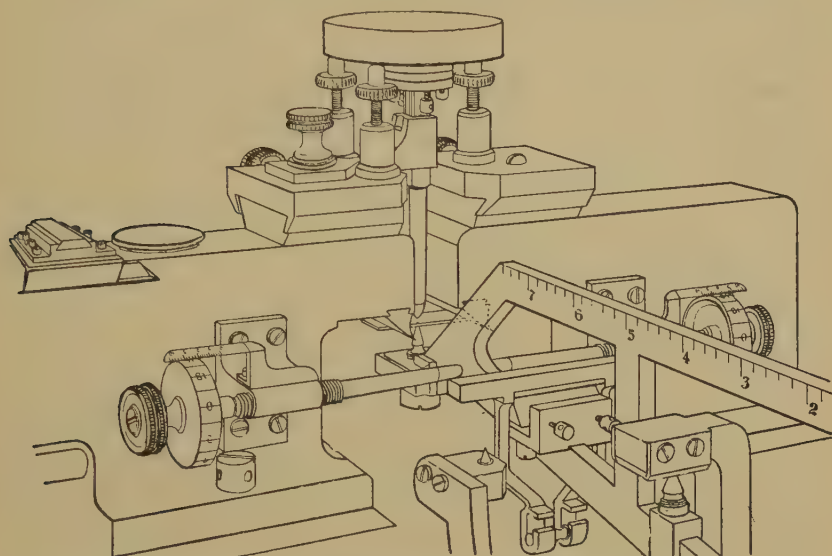


FIG. 27.—The Platinum-Iridium Wedges, Crystal-plate, Balance and its Pressure-point, and Interference Apparatus of Elasmometer.

first coarsely and subsequently very finely, until a hook, carried by the special form of weight instead of a knob, comes to rest in a loop of string suspended from the upper bar of the pan-fitting. To steady the balance during all these operations, the pan carries a second pan underneath it, parallel to it and at some little distance, connected by a rigid central rod. This lower pan is immersed in a dish of cedar oil during the determinations, which effectually steadies the bands and prevents all flickering, while barely at all affecting the sensibility of the balance. A counter-

poise is fitted to the other side of the balance to compensate for the alteration of the weight by the introduction of this steadying device. When all preliminaries have been carried out, the crystal and pressure point being adjusted and a little initial weight put on, sufficient just slightly to bend the bar and thus to be sure of perfect contact, one begins the determination by working the coarse movement of the control so as to let down the weight very slowly into the string loop, watching the interference bands all the time to see that no movement yet occurs from the initial adjusted position. As the loop becomes taut with the advent of the weight-hook, one will observe a commencement of motion on the part of the bands; as soon as this occurs the fine movement is resorted to. The motion of the bands will then gradually become more pronounced, until they are eventually slowly and steadily marching past the reference mark. One continues the very slow procession by still lowering the weight with the fine movement, counting carefully all the time as each band passes the silver-ring-centre, until, as the weight comes to be fully suspended and hanging freely from the loop, the supporting table being now withdrawn free of it, the bands eventually come completely to rest again, and the experiment is finished as regards the bending. But it is possible now to reverse the process, and to take up the weight again on the little table of the control apparatus, to cause the bands to retrace their steps, and eventually to come to rest again, with the weight clear of the loop and fully supported on its little stand, the table of which is cloth covered and projects over rigidly into the space above the centre of the pan. The two experiments should agree perfectly to a small fraction of a band. The initial and final fractions in each experiment are, of course, determined micrometrically at the start and conclusion. To avoid resetting the delicate balance after each experiment, two milled-headed guide screws with divided silver drums

and ivory tips are provided (seen in Fig. 27), for the adjustment of the beam end near the pressure point, which are withdrawn during each experiment, and then screwed up again to the readings for perfect adjustment of the beam end, and then once more withdrawn.

There is also provided a delicate measuring microscope, seen on the left, which enables the dimensions of the bar or plate of crystal to be accurately determined *in situ*. The whole instrument is very efficient, and the interference bands are remarkably steady in their movement, rendering their counting quite easy.

The Universal Interferometer.—It was highly desirable that the method of measurement by light waves, which had been so successfully applied to the determination of thermal expansion and Young's modulus of elasticity in the case of crystals and small bodies in general, should also be applied to the determination of the torsion coefficients of crystals, and thus complete the cycle of operations necessary for calculation of all the elastic constants of crystals, even in cases of low symmetry. Moreover, there are other properties of crystals, such as the deformation suffered on electrification, the so-called piezo-electric effect, and it was considered very desirable to devise an instrument which would be of general application in the determination of all such small movements or short distances. Experience gained by the author in employing the wavelength method for the comparison of the Imperial standards of length with copies, enabled the following instrument to be devised, and it has proved to serve the purpose admirably. It is shown in Fig. 28 as seen from the front, and in Fig. 29 from the side.

The principle on which the interference bands are produced is the same as for the dilatometer and elasmometer, and the same auto-collimation telescope is used, but mounted on a different pedestal, which is part of the new instrument. The essential new feature is that the black

glass disc, the polished surface of which forms one of the two surfaces reflecting the interfering rays, is carried by and rigidly attached to a travelling microscope, the

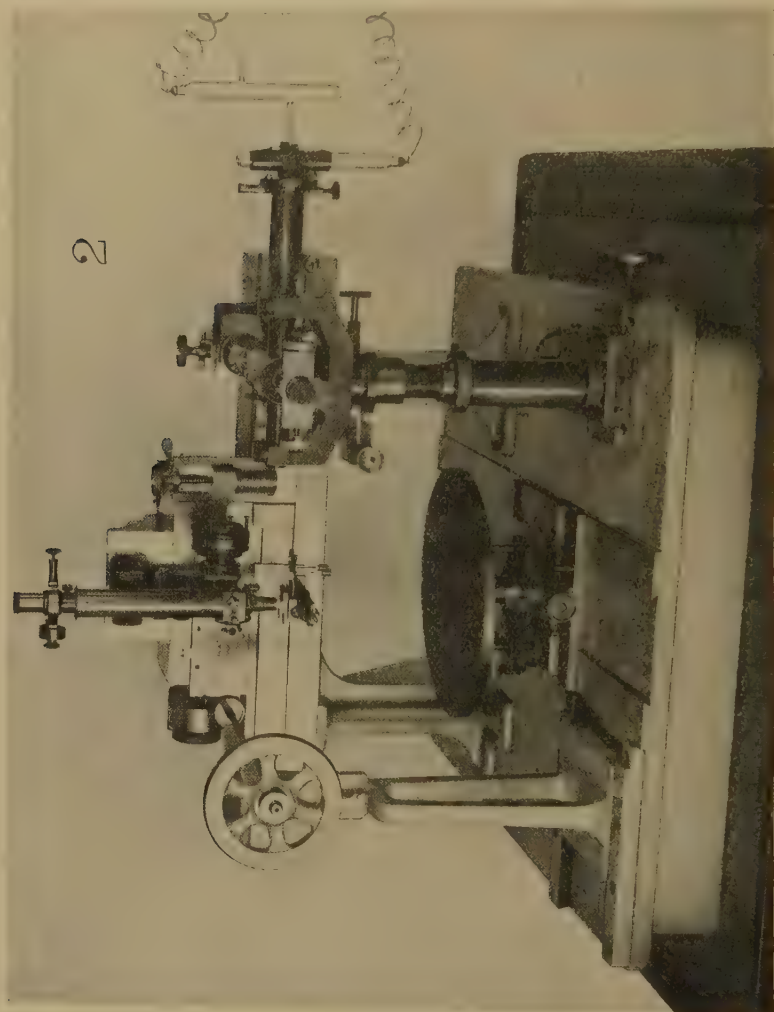


Fig. 28.—The Universal Interferometer.

reflecting surface being now vertical, parallel to the microscope axis. The microscope is rigid with a stout cast-iron slab, which slides horizontally, parallel to itself, with V-and-plane contact, over a thicker block of steel, the

movement being effected by a fine screw, on which immense care has been bestowed, of one-fiftieth inch pitch, the screw

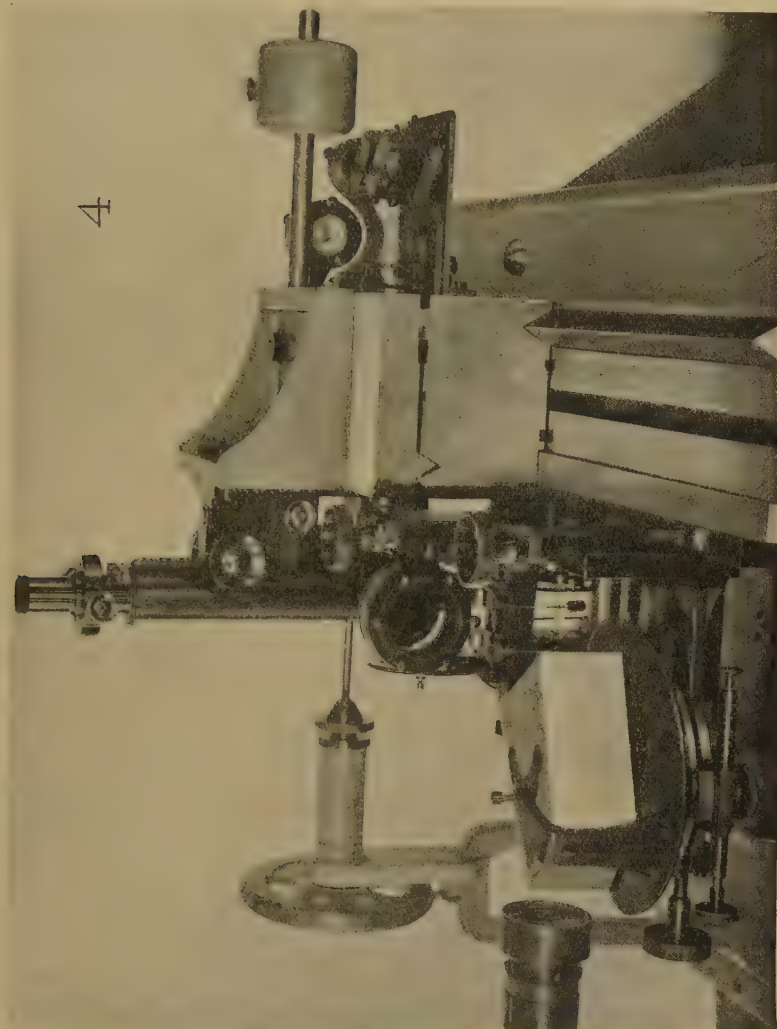


Fig. 29—Universal Interferometer (with Torsometer), side view.

and the V-and-plane being so true that the interference bands remain perfectly adjusted, and move steadily parallel to themselves, when the screw is worked. The steel block in turn moves similarly over a cast-iron V-and-plane bed

which is also horizontal and thirty inches long, and affords the coarse adjustment of the microscope to the convenient position along it, and also serves for the attachment of the dispersion and interference apparatus, which in this instrument are arranged horizontally; that is, the axis of the rays lies entirely in the horizontal plane, being bent at right angles as in the other two instruments, but in the horizontal instead of the vertical plane. The telescope is arranged exactly as in the dilatometer and elasmometer, horizontally.

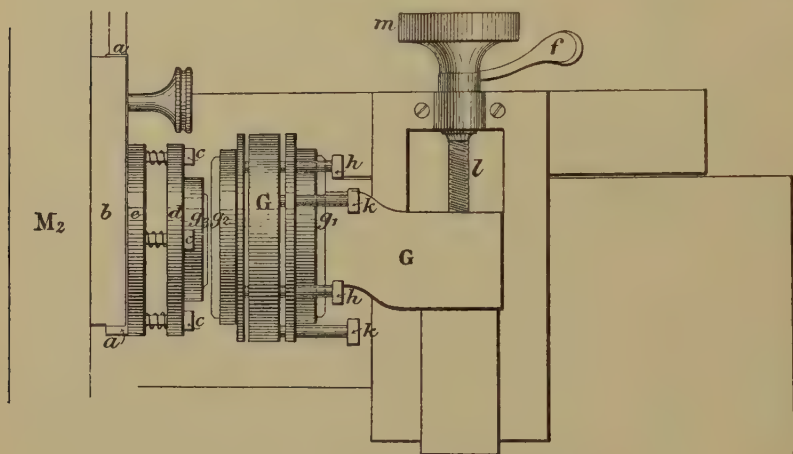


FIG. 30.—The Interference Discs.

But the dispersion apparatus is now a constant deviation (90°) prism of large size (made by Hilger), and is arranged horizontally, being accommodated on a rotating table carried by an arm projected from a stout fitting sliding to the convenient position opposite the telescope stiffly along a dove-tail groove made in the front of the long iron bed. A second arm and slider carry the interference discs, two (duplicate) colourless glass plates, really wedges of thirty minutes angle, serving the same purpose as the cover-glass wedge-disc of the tripod of the dilatometer and elasmometer, and its duplicate countervailing wedge-disc. They are mounted with the surfaces vertical, parallel and close to

the black glass surface carried by the microscope. The nearest colourless glass surface is about a millimeter removed from the black glass surface. The latter is three centimetres in diameter, and the colourless discs five centimetres, and one centimetre thick. All five surfaces are true-plane polished. Their arrangement is shown in the accompanying drawing, Fig. 30.

The fine screw which drives the microscope and black glass surface carries at its outer end, first a large milled head for direct hand rotation; next to which comes a large silver drum with eleven circles at equidistant positions along it and all parallel to each other, the two outermost being divided directly into a hundred parts; by a corresponding number of oblique lines drawn from the points of the division to the next point on the other outer circle, and an indicating axially parallel line on a glass window, the thousandths of a rotation, that is, the fifty-thousandths of an inch, are directly readable. But hand movement of the screw is only useful for coarse movements, the bands flashing past the reference mark of the telescope. So the fine movement of the microscope and black glass surface is effected by an endless screw, manipulated by the large wheel shown on the left in the illustration, which gears up to the endless screw by a flexible-coil steel shaft (which is just the thing to avoid strain, here so much to be deprecated). The endless screw in turn gears with a worm-wheel of a hundred teeth, cut next after the drum-head on the outer part of the screw shaft. A complete revolution of the big wheel (by the left hand) advances the microscope and black glass surface by one-five-thousandth of an inch or 0.005 millimetre, and causes fifteen interference bands in red hydrogen light to pass the reference centre, so that about 24° of rotation of the wheel corresponds to the passage of each band. The movement is remarkably steady, and ceases the moment the wheel stops. Any band can be held on the reference centre as long as may be

desired. This happy result is largely owing to the weight of the sliding block, the microscope, and its counterpoise, being relieved to the extent of nine-tenths of the whole by four spring-pistons terminating in steel ball-bearing rollers of over three centimetres diameter, thus leaving only one-tenth of the weight to be moved.

The object of the microscope is to focus, and to follow up, the motion of a little slider bearing a fine fiducial mark, the actual object which is the subject of the experiment being caused to push the slider along in effecting its own movement, the slider moving over a miniature V-and-plane bed frictionless at the least touch. For instance, in the case of the torsometer to be described in the next section, and which has formed the first practical application of the universal interferometer, the slider is caused to be pushed along by a lever attached to the crystal bar near its end, as torsion is applied. Indeed, for the convenience of the torsometer application, two such little sliders are provided, one being pushed by a lever attached to the bar near one end, and the other by a similar lever near the other end of the bar, according to the usually employed method of torsion determination on the large scale.

The fiducial mark employed is an interesting one, the finest ever used. Previous experience with the fiducial marks on the Imperial standards of length and those at Sèvres showed that the finest scratch used as fiducial mark, one made by M. Benoit on our platinum-iridium yard and corresponding to a similar one on the French State metre, is of a thickness corresponding to fifteen interference bands. The fiducial mark now used in this interferometer contains only two half-wave-length bands in its width. It is composed of five lines one forty-thousandth of an inch apart, the wave-length of red light, the middle one of the five being the actual reference mark, the other four aiding in finding and defining it. It is shown in Fig. 31. These

five lines were ruled on a miniature slab of speculum metal by the late Prof. Grayson of Melbourne, and are wonderfully sharp and clear under the resolution provided by the microscope, the latter having been specially dealt with by Mr. Conrad Beck. A specially calculated one-sixth inch apochromatic objective of 0.95 aperture, with a special eyepiece magnifying 50 times is used, affording a combination which gives a magnification of three thousand diameters, and superior resolution to an ordinary one-

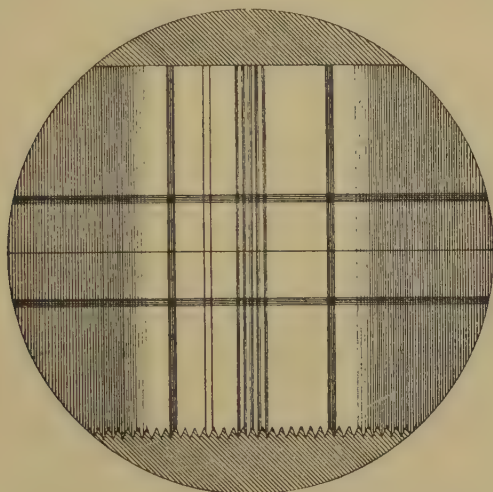


FIG. 31.—The Grayson Ruling Fiducial Mark.

fifteenth objective, while leaving a very appreciable working distance, equal to the thickness of a thick card.

The interesting thing about these rulings, fine scratches with a diamond tetrahedron point on speculum metal, is that, their separation being only that of a wave-length of light, they can be seen at all. Even one of the very latest books dealing with microscopic vision states that when the order of size of object is that of a wave-length of light it cannot be seen by any power of a microscope. But here are sharp lines of wave-length dimensions clearly focussed, and indeed Prof. Grayson ruled lines up to the 150,000th

of an inch, and Mr. Beck has resolved even these, but of course with some difficulty.

The markings on *amphipleura pellucida*, the diatom usually employed to test microscopic resolution, are about the 120,000th inch apart, and lines of this separation are quite clearly resolved by the author's microscope. Hence, the rulings of only the one forty-thousandth of an inch are not only feasible as fiducial marks, but practical. Prof. Grayson ruled the four coarser lines (two horizontal and two vertical) also seen in Fig. 31, as finder lines for preliminary use with a lower power. The two thin parallel vertical lines in the figure are the spider lines of the micrometer eyepiece, one of which can be moved separately in order to adjust their separation so as to be able to enclose the middle (third) line, the "signal," between them. The horizontal spider line enables centring and parallelism in all operations to be maintained and governed.

The arrangement of the observing telescope to the right, and the big wheel driving apparatus on the left, enables the central front part of the apparatus to be free for the accommodation of the "work." Whatever is brought up for measurement is placed on the central round gun-metal table, which is provided with every needful adjustment, two horizontal movements at right angles, a rotatory movement in its own plane, and vertical movement by relatively long levelling screws.

The fitting carrying the two little sliders, with their centimetre square speculum metal slabs on which the rulings are engraved, is mounted adjustably in the same grooved (dove-tailed) guide, in the front of the big V-and-plane bed, as the dispersion and interference apparatus. It has movements for adjusting both the separation and the simultaneous movement of the V-and-plane slider supports. The fitting can thus be very readily removed altogether, for it will not be every piece of "work" that needs it, as the thing to be measured may carry its own

fiducial mark. They are needed, however, for the first application of this new interferometer, that of the torsometer.

The Torsometer.—This little apparatus, for determining

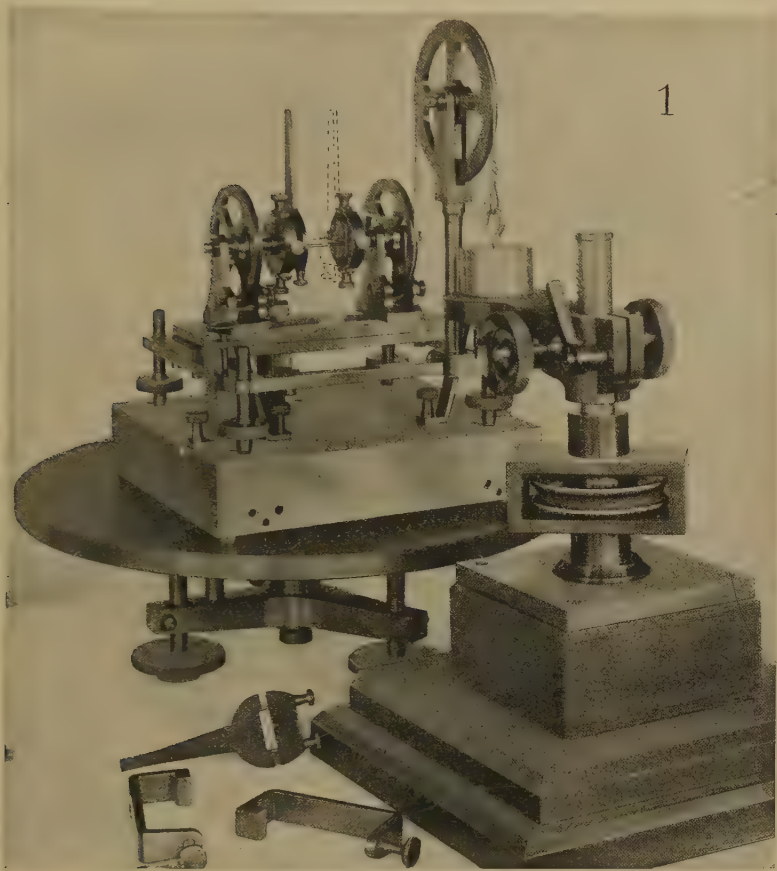


FIG. 32.—The Torsometer.

the torsion coefficients of crystals or other small bodies unobtainable in bulk (rare metals, for instance), is a refinement of the torsion apparatus of the late Prof. Voigt of Göttingen, who used two optical levers to determine the torsion at the two ends of the bar. It is also designed

on the principle of the ordinary engineering laboratory grosser method, used with iron or steel or other metals readily obtained in large bars. The construction will be evident from the figure (Fig. 32).

The little crystal bar is held at each end by a gripping chuck, carried at the end of a short cylindrical bearing which at its outer end carries rigidly with it a large pulley, mounted frictionless in cone-axles, for use with a band and a still larger pulley-wheel in applying the torsion. The chuck in each case is provided with safety devices to prevent crushing of the crystal, and for adjusting the bar axis to the axis of the instrument. The larger pulley, over which the band passes to the weight, may be arranged opposite to the pulley at either end, its columnar support sliding on a stout bar, so that the torsion may be delivered at both ends in turn, the other pulley of the smaller pair being fixed by two binding screws during the delivery of the torsion couple (twist) at the other end. The weight can be lowered into the loop of the band by its hook, with the aid, if required, of the coarse movement of the same weight-lowering apparatus as is used in the elasmometer, so as to prevent jerks, which are liable to break the crystal bar.

The arrangement for transmitting the torsion movement to the interferometer consists of two radials of aluminium, one gripping the bar near each end, as close as can be to the chuck without actual contact therewith. The expanded gripping part has a somewhat blunted knife-edge where it makes contact with the bar, and this does not press actually into the bar itself, which it might injure in the case of a rather soft crystal, but into a strip of tin foil the same length as the bar and laid along it. This tin-foil strip bearing the clean impress of the two knife edges of the two radials, can afterwards be used for the measurement of the effective length of the bar twisted, that between the two mark-impressions, a device due to Voigt. Each

radial is intended to press against one of the little slides, carrying the Grayson-ruling fiducial marks, of the interferometer, as described in the preceding section. The torsometer is placed in position on the adjusting table of the interferometer, as shown in Figs. 29 and 32, conveniently for this function, the adjustment of the round table for height being such as brings the short knife-edge outer ends of the sliders (their other ends being attached to the little counterpoising weight by a flexible string passing over a small pulley supported by the fitting) about three millimetres below the upper free ends of the radials. The torsometer is, of course, arranged with its axis (the crystal bar-axis) horizontal and perpendicular to the long *V*-and-plane bed of the interferometer.

When everything has been adjusted, the application of torsion to the crystal bar can be commenced, by gently lowering the weight-supporting table until the hook of the weight rests in the string loop, the observer looking through the microscope all the time and observing the movement of the signal-rulings as the radial, in moving with the bar, pushes the slider along its bed. If the weight is more than 100 grammes, the rulings will probably have passed out of the field. As soon as the full amount of torsion has been applied, the weight hanging freely from the loop, the weight can be taken up again on its table, without any movement of the rulings, as release of the torsion causes the radial to recede from contact with the slider. It only then remains to follow the rulings, from their initial adjusted position centred under the microscope when the radial was just in complete contact with the slider at the beginning of the operation, to the changed position caused by the torsion. This is done by rotating the big wheel which drives the microscope, and counting the interference bands as they pass the reference centre of the telescope. The speed of the bands can be as slow as may be desired, and the microscope can be consulted as often as

needed without losing count, until at the finish the rulings are again finally centred, and the final fraction of a band, if any, is measured with the micrometer. A similar set of operations can then be carried out for the second radial and slider, the adjustments enabling it to be brought quite readily under the microscope. Indeed, it is really not absolutely necessary to have a second slider for the other end of the bar, as the observations at the two ends can be carried out as two separate experiments, using one and the same slider, and moving the big round table with the whole torsometer for each observation to the position of the single slider, which then is always ready under the microscope. Experience shows that the results afford the same mean value for the torsion in the end. After the pair of observations for one arrangement of the large pulley have been completed, it can be transferred to the other end of the torsometer, and the torsion applied at that other end, releasing the smaller pulley at this end and fixing the other one instead. The torsion produced at the fixed end is never negligible, and always requires to be determined, and deducted from the result at the other end where the torsion is applied.

CHAPTER IV

THE RESEARCH ON THE ALKALI SULPHATES AND SELENATES

Conditions for Good Crystals.—Perhaps the most important thing of all in such a research, where the expected angular differences between the salts compared were sure to be small, was to obtain crystals as near perfection as possible, with faces truly plane, bright and unstriated or otherwise undistorted, affording clearly-defined single images of the collimator signal-slit of the goniometer. Without such perfect crystals all the refined methods of measurement, and the delicate new apparatus which has been described, would be of no avail. It is not by any means every relatively slow crystallisation that affords such crystals, and frequently many preparations have to be made before such can be found, and even then perhaps only a very few out of the whole crop are adequately good.

The work of Ostwald, and especially the later experimental work of Sir Henry Miers, has established what are the favourable conditions. They have shown that there are two stages of supersaturation, with a sharp limit between them, the “metastable” and the “labile” stages. Metastable supersaturated solutions are not spontaneously crystallisable, it being necessary to start the crystallisation by throwing in a crystal of the substance or one closely isomorphous, isostructural, with it; or else for a minute crystal of this same nature to fall into it from the air, where it had already been shown by Violette and Gernez independently that such minute crystal germs of most common substances exist, and which have been determined by Macintosh to be so small as to weigh no more and often less than 10^{-8} gramme (one hundred millionth).

But labile supersaturated solutions do spontaneously crystallise, without the need for the introduction of a visible or invisible crystal of the same sort to start the crystallisation. If a "Solubility Curve" be constructed by plotting concentration of solution against temperature for a just saturated solution, then the curve of supersolubility lies usually approximately parallel to the solubility curve.

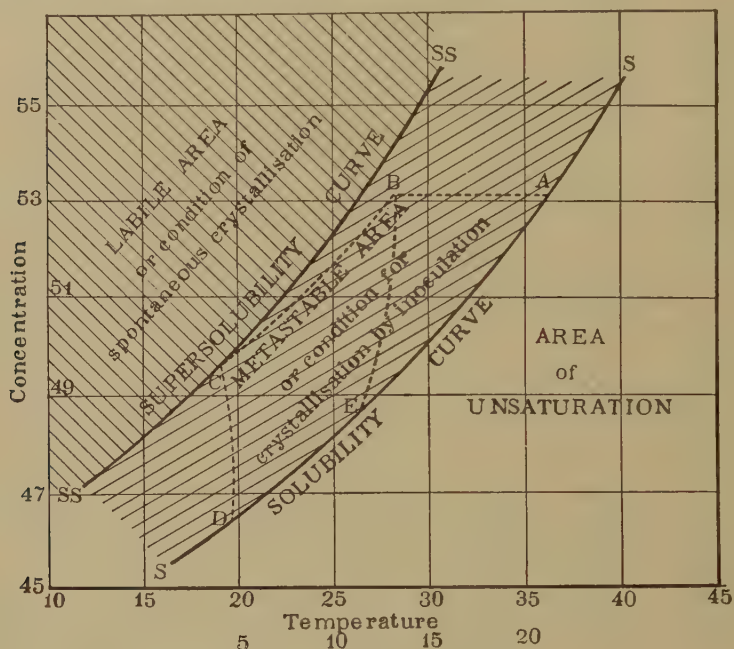


FIG. 33.—Solubility Curves.

bility curve at a distance about 10° from it. The area between the two curves is that corresponding to the metastable condition. That beyond the supersolubility curve is the region corresponding to the labile condition. Fig. 33 will render this clear.

If a strongly supersaturated solution be made by adding the salt to hot water, and it be stirred while cooling, no crystals are deposited until the metastable area has been well entered, when a slight shower falls and continues to

be deposited slowly, until the same 10° lower temperature of the supersolubility curve has been reached, when the labile condition is attained and practically the whole of the excess of salt is deposited at once as a cloud of crystals. These crystals, being so rapidly formed, and the solution being stirred and thus disturbed, are of course not sufficiently perfect for use in crystallographic research. The conditions for the deposition of good crystals are that only a slightly supersaturated solution shall be prepared, which shall be in the metastable state only from the first. On setting such a solution to rest overnight, in a quiet protected place, crystallisation is eventually set going by inoculation with a germ-crystal from the air, and proceeds slowly but steadily during the night while the temperature is lowering and also slow evaporation occurring; the labile condition is never reached, and next morning a crop of good crystals is probably obtained, in which there may very likely be some particularly excellent individuals suitable for the research. In this manner have been grown the crystals employed in the researches on the sulphates, selenates, and double salts, which are now to be described.

The Relationship of the Alkali Metals.—The alkali metals potassium, rubidium, and caesium are particularly suitable as the interchangeable elements of the isomorphous series to be studied. For they belong to the same family group, and indeed, to the same (even) series of that group, Group 1 and Series 4, 6, and 8 of that group of the periodic classification of the elements. They are very strongly electropositive, caesium being the most electropositive element known. Their atomic numbers (sequence numbers in the periodic table) are 19, 37, and 55, there being an interval of 18 between both potassium and rubidium, and between the latter and caesium. Their atomic weights are similarly related, being 38.9, 84.9, and 131.9 respectively, that of rubidium being almost exactly the mean (85.4) of the atomic weights of potassium and caesium. Hence, the kind of

difference in the interfacial angles and physical constants of the crystals of the salts containing these three metals respectively, which might be supposed to be possible and probable, should make itself very clear, and well removed from any experimental or formational error. Besides these reasons, and the fact that the salts crystallise splendidly, other reasons dependent on the structure of

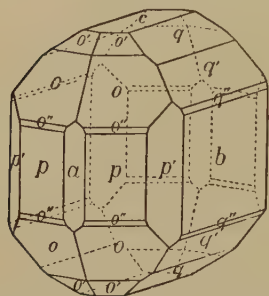


FIG. 34.—Potassium Sulphate.

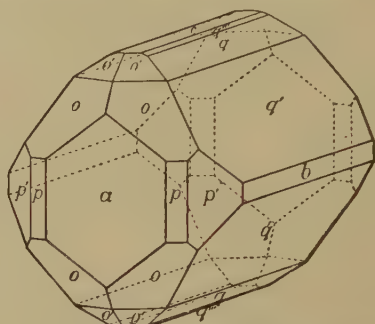


FIG. 35.—Rubidium Sulphate.

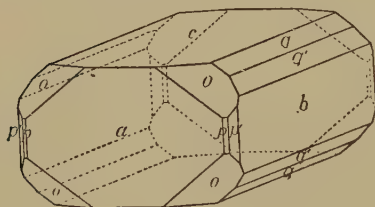


FIG. 36.—Cæsium Sulphate.

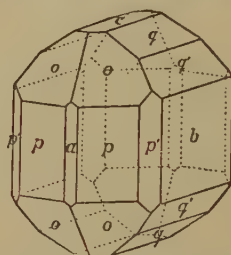


FIG. 37.—Ammonium Sulphate.

the atoms of these alkali metals will be indicated later, and all emphasise the fortunate nature of the choice of the salts of these metals for the research.

External Characters of the Sulphates.—Characteristic crystals of the five anhydrous rhombic sulphates of potassium, rubidium, cæsium, ammonium, and thallium are shown in Figs. 34 to 38, and their common stereographic projection in Fig. 39.

A comparative list of their interfacial angles is given in the accompanying table. This is followed by a little table

Table of Angles of Alkali Sulphates.

Angle.	K ₂ SO ₄ .	Rb ₂ SO ₄ .	Cs ₂ SO ₄ .	(NH ₄) ₂ SO ₄ .	Tl ₂ SO ₄ .
$\begin{cases} ap = (100) : (110) \\ pp' = (110) : (130) \\ p'b = (130) : (010) \end{cases}$	$\begin{matrix} 29^{\circ} & 48' \\ 30 & 0 \\ 30 & 12 \end{matrix}$	$\begin{matrix} 29^{\circ} & 47' \\ 30 & 0 \\ 30 & 13 \end{matrix}$	$\begin{matrix} 29^{\circ} & 44' \\ 30 & 0 \\ 30 & 16 \end{matrix}$	$\begin{matrix} 29^{\circ} & 24' \\ 30 & 0 \\ 30 & 36 \end{matrix}$	$\begin{matrix} 29^{\circ} & 3' \\ 29 & 59 \\ 30 & 58 \end{matrix}$
$\begin{cases} cq''' = (001) : (012) \\ q'''q = (012) : (011) \\ cq = (001) : (011) \\ qq' = (011) : (021) \\ q'q'' = (021) : (031) \\ q''b = (031) : (010) \\ q'b = (021) : (010) \end{cases}$	$\begin{matrix} 20 & 21 \\ 16 & 13 \\ 36 & 34 \\ 19 & 27 \\ 9 & 47 \\ 24 & 12 \\ 33 & 59 \end{matrix}$	$\begin{matrix} 20 & 31 \\ 16 & 18 \\ 36 & 49 \\ 19 & 26 \\ 9 & 45 \\ 24 & 0 \\ 33 & 45 \end{matrix}$	$\begin{matrix} 20 & 38 \\ 16 & 21 \\ 36 & 59 \\ 19 & 26 \\ 9 & 42 \\ 23 & 53 \\ 33 & 35 \end{matrix}$	$\begin{matrix} 20 & 6 \\ 16 & 6 \\ 36 & 12 \\ 19 & 28 \\ 9 & 51 \\ 24 & 29 \\ 34 & 20 \end{matrix}$	$\begin{matrix} 20 & 7 \\ 16 & 7 \\ 36 & 14 \\ 19 & 28 \\ 9 & 50 \\ 24 & 28 \\ 34 & 18 \end{matrix}$
$\begin{cases} ao = (100) : (111) \\ oq = (111) : (011) \end{cases}$	$\begin{matrix} 43 & 52 \\ 46 & 8 \end{matrix}$	$\begin{matrix} 43 & 41 \\ 46 & 19 \end{matrix}$	$\begin{matrix} 43 & 31 \\ 46 & 29 \end{matrix}$	$\begin{matrix} 43 & 39 \\ 46 & 21 \end{matrix}$	$\begin{matrix} 43 & 13 \\ 46 & 47 \end{matrix}$
$\begin{cases} ao' = (100) : (112) \\ o'o' = (112) : (\bar{1}12) \end{cases}$	$\begin{matrix} 58 & 44 \\ 62 & 32 \end{matrix}$	$\begin{matrix} 58 & 31 \\ 62 & 58 \end{matrix}$	$\begin{matrix} 58 & 19 \\ 63 & 22 \end{matrix}$	$\begin{matrix} 58 & 37 \\ 62 & 46 \end{matrix}$	$\begin{matrix} 58 & 14 \\ 63 & 32 \end{matrix}$
$\begin{cases} bo = (010) : (111) \\ oo = (111) : (\bar{1}\bar{1}1) \end{cases}$	$\begin{matrix} 65 & 37 \\ 48 & 46 \end{matrix}$	$\begin{matrix} 65 & 33 \\ 48 & 54 \end{matrix}$	$\begin{matrix} 65 & 32 \\ 48 & 56 \end{matrix}$	$\begin{matrix} 65 & 56 \\ 48 & 8 \end{matrix}$	$\begin{matrix} 66 & 7 \\ 47 & 46 \end{matrix}$
$\begin{cases} bo' = (010) : (112) \\ o'o' = (112) : (\bar{1}\bar{1}2) \end{cases}$	$\begin{matrix} 72 & 42 \\ 34 & 36 \end{matrix}$	$\begin{matrix} 72 & 37 \\ 34 & 46 \end{matrix}$	$\begin{matrix} 72 & 33 \\ 34 & 54 \end{matrix}$	$\begin{matrix} 72 & 56 \\ 34 & 8 \end{matrix}$	$\begin{matrix} 73 & 0 \\ 34 & 0 \end{matrix}$
$\begin{cases} co' = (001) : (112) \\ o'o = (112) : (111) \\ co = (001) : (111) \\ oo'' = (111) : (332) \\ o''p = (332) : (110) \\ op = (111) : (110) \end{cases}$	$\begin{matrix} 36 & 44 \\ 19 & 27 \\ 56 & 11 \\ 9 & 45 \\ 24 & 4 \\ 33 & 49 \end{matrix}$	$\begin{matrix} 37 & 0 \\ 19 & 26 \\ 56 & 26 \\ 9 & 42 \\ 23 & 52 \\ 33 & 34 \end{matrix}$	$\begin{matrix} 37 & 13 \\ 19 & 25 \\ 56 & 38 \\ 9 & 40 \\ 23 & 42 \\ 33 & 22 \end{matrix}$	$\begin{matrix} 36 & 42 \\ 19 & 27 \\ 56 & 9 \\ 9 & 46 \\ 24 & 5 \\ 33 & 51 \end{matrix}$	$\begin{matrix} 37 & 2 \\ 19 & 26 \\ 56 & 28 \\ 9 & 42 \\ 23 & 50 \\ 33 & 32 \end{matrix}$
$\begin{cases} po = (110) : (\bar{1}\bar{1}1) \\ oq' = (\bar{1}\bar{1}1) : (021) \\ q'p = (021) : (\bar{1}10) \end{cases}$	$\begin{matrix} 65 & 8 \\ 49 & 12 \\ 65 & 40 \end{matrix}$	$\begin{matrix} 65 & 2 \\ 49 & 22 \\ 65 & 36 \end{matrix}$	$\begin{matrix} 64 & 54 \\ 49 & 30 \\ 65 & 36 \end{matrix}$	$\begin{matrix} 64 & 31 \\ 49 & 24 \\ 66 & 5 \end{matrix}$	$\begin{matrix} 63 & 52 \\ 49 & 47 \\ 66 & 21 \end{matrix}$
$\begin{cases} po' = (110) : (\bar{1}\bar{1}2) \\ o'q = (\bar{1}\bar{1}2) : (0\bar{1}1) \\ qp = (0\bar{1}1) : (\bar{1}\bar{1}0) \end{cases}$	$\begin{matrix} 72 & 23 \\ 34 & 50 \\ 72 & 47 \end{matrix}$	$\begin{matrix} 72 & 15 \\ 35 & 4 \\ 72 & 41 \end{matrix}$	$\begin{matrix} 72 & 7 \\ 35 & 15 \\ 72 & 38 \end{matrix}$	$\begin{matrix} 71 & 58 \\ 34 & 53 \\ 73 & 9 \end{matrix}$	$\begin{matrix} 71 & 27 \\ 35 & 14 \\ 73 & 19 \end{matrix}$
$\begin{cases} p'o = (130) : (111) \\ oo' = (111) : (\bar{1}\bar{1}2) \\ o'q' = (\bar{1}\bar{1}2) : (021) \\ q'p' = (021) : (\bar{1}30) \end{cases}$	$\begin{matrix} 43 & 59 \\ 45 & 47 \\ 46 & 1 \\ 44 & 13 \end{matrix}$	$\begin{matrix} 43 & 49 \\ 45 & 55 \\ 46 & 12 \\ 44 & 4 \end{matrix}$	$\begin{matrix} 43 & 40 \\ 46 & 1 \\ 46 & 20 \\ 43 & 59 \end{matrix}$	$\begin{matrix} 44 & 0 \\ 45 & 16 \\ 46 & 1 \\ 44 & 43 \end{matrix}$	$\begin{matrix} 43 & 47 \\ 45 & 3 \\ 46 & 16 \\ 44 & 54 \end{matrix}$
$\begin{cases} p'o' = (130) : (112) \\ o'q = (\bar{1}\bar{1}2) : (011) \\ qp' = (0\bar{1}1) : (\bar{1}30) \end{cases}$	$\begin{matrix} 58 & 48 \\ 62 & 12 \\ 59 & 0 \end{matrix}$	$\begin{matrix} 58 & 35 \\ 62 & 36 \\ 58 & 49 \end{matrix}$	$\begin{matrix} 58 & 25 \\ 62 & 53 \\ 58 & 42 \end{matrix}$	$\begin{matrix} 58 & 50 \\ 61 & 43 \\ 59 & 27 \end{matrix}$	$\begin{matrix} 58 & 33 \\ 61 & 54 \\ 59 & 33 \end{matrix}$

Average and Maximum Angular Changes.

Rhombic Series of Alkali Sulphates.

For replacement of	Average Change.	Maximum Change.
K in K_2SO_4 by Rb	$0^\circ 9'$	$0^\circ 26'$
" " Cs	$0 17$	$0 50$
" " NH_4	$0 14$	$0 38$
" " Tl	$0 27$	$1 16$

in which the results are analysed in a convenient manner for showing clearly the nature of the differences. The whole of the differences for any particular replacement of one alkali metal or base by another or by thallium have been worked out and the mean taken.

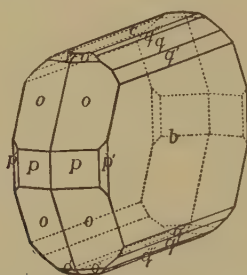


FIG. 38.—Thallium Sulphate.

The first striking fact observed is that the whole of the interfacial angles of rubidium sulphate are, without exception, intermediate between the analogous angles of the potassium and caesium salts. The second is that both the average and the maximum observed change of angle for the replacement of potassium by caesium is exactly double that for the interchange of rubidium for potassium. Hence the changes are, on the average or at their greatest, exactly proportional to the change in atomic number or atomic weight, when one alkali metal is replaced by another.

for the ammonium substitution, and greater than for the caesium substitution. The axial ratios, $a:b:c = 0.5555:1:0.7328$, are still of the same order as for the other four salts. So that in the case of thallium sulphate also close isomorphism is indicated, but with no reference to atomic weight or atomic number, which in the case of thallium is very high, 202.6 atomic weight and 81 atomic number.

The Structural Constants.—It was while the investigation of these alkali sulphates was in progress that Prof. Becke of Prague suggested in a letter to the author, that relative measures of the dimensions of the crystal unit, the cell of the space-lattice, might be obtained by combining the axial ratios with the molecular volume, the latter being the well-known quotient of the molecular weight by the density of the crystals. For the type of structure (space-lattice) in an isomorphous series, and the number of molecules which go to the unit cell of the latter, must be the same for all the members of the series, so that the results will be strictly comparable. The author at once adopted the suggestion, and made particularly careful determinations of the densities of the crystals of all the salts investigated so as to be able to calculate the molecular volume.

About the same time, quite unknown to the author, Prof. Muthmann also adopted a similar suggestion by Prof. Becke, in connection with an investigation of some permanganates, and he called the new space ratios "topic axial ratios." The author called them "molecular distance ratios," as "topic" had already another significance in the English language, and the ratios more correctly represent the relative distances apart of the molecular or polymolecular unit-cell centres in the three directions of space. The term "topic axial ratios," however, has become current and so can now be adopted, so long as the nature of the ratios is clearly understood.

If V be the molecular volume, afforded by molecular weight density (sp. gr.), and χ, ψ, ω be the three topic axial ratios, corresponding to the three crystal axial directions, a, b, c being the crystal-axial ratios, and α, β, γ the crystal-axial angles, then the new ratios are expressed by the following formulæ, in the most general case, that of a triclinic crystal :—

$$\chi = \sqrt[3]{\frac{a^2 V}{c \sin \beta \cdot \sin \gamma \cdot \sin \theta}},$$

$$\psi = \sqrt[3]{\frac{V}{ac \sin \beta \cdot \sin \gamma \cdot \sin \theta}},$$

$$\omega = \sqrt[3]{\frac{c^2 V}{a \sin \beta \cdot \sin \gamma \cdot \sin \theta}}.$$

The angle θ is such that

$$\sin \frac{\theta}{2} = \frac{\sin (s - \beta) \sin (s - \gamma)}{\sin \beta \sin \gamma}, \text{ where } s = \frac{\alpha + \beta + \gamma}{2}.$$

These formulæ simplify, more and more, as symmetry is introduced. For a monoclinic crystal, as α, γ , and θ are right angles and $\sin 90^\circ = 1$, they reduce to :—

$$\chi = \sqrt[3]{\frac{a^2 V}{c \sin \beta}}, \psi = \sqrt[3]{\frac{V}{ac \sin \beta}}, \omega = \sqrt[3]{\frac{c^2 V}{a \sin \beta}}.$$

These formulæ were used in 1896 and subsequently, for the monoclinic double sulphates. For a rhombic crystal they become :—

$$\chi = \sqrt[3]{\frac{a^2 V}{c}}, \psi = \sqrt[3]{\frac{V}{ac}}, \omega = \sqrt[3]{\frac{c^2 V}{a}}.$$

These were the formulæ used in 1894 for the rhombic

sulphates now under discussion. For a tetragonal crystal they reduce further to :—

$$\chi = \psi = \sqrt[3]{\frac{V}{c}}, \quad \omega = \sqrt[3]{c^2 V}.$$

Eventually for a cubic crystal they become

$$\chi = \psi = \omega = \sqrt[3]{V}.$$

In the next table are given the results for the rhombic sulphates. Besides the set of ratios obtained directly by the use of the formulæ, another set is appended in which the value of ψ for the sulphate of potassium, the initial salt of the series, is taken as unity, so as to bring out the progression more clearly.

Table of Topic Axial Ratios.

Salt.	Molecular Volume.	Direct results of formulæ.	ψ for $K_2SO_4 = 1.$
		$\chi : \psi : \omega.$	$\chi : \psi : \omega.$
K_2SO_4 .	64.91	3.0617 : 5.3460 : 3.9657	0.5727 : 1.0000 : 0.7418
Rb_2SO_4 .	73.34	3.1778 : 5.5528 : 4.1562	0.5944 : 1.0387 : 0.7774
$(NH_4)_2SO_4$.	74.04	3.1788 : 5.6413 : 4.1289	0.5946 : 1.0552 : 0.7723
Cs_2SO_4 .	84.58	3.3215 : 5.8149 : 4.3792	0.6213 : 1.0877 : 0.8191

From this table it will be clear that a similar progression according to atomic number and weight is observed in the volumes and edge-dimensions of the space-lattice unit cells of the three sulphates of the alkali metals, as was observed with respect to their interfacial angles, the volume and edge-lengths of the rubidium salt being intermediate between the volumes and edges of the cells of the potassium and cæsium salts. With regard to the structural constants for the ammonium salt, they are almost identical with the corresponding constants of the rubidium salt. This is particularly interesting, as it means that the ammonium salt and the rubidium salt are very closely

isostructural. Also, in spite of the enormously greater density of thallium sulphate, the cell-volume and cell-edges of this salt are also very nearly the same as those of the rubidium salt.

It has been expressly made clear that these constants, molecular volume and topic axial ratios, are relative measures. But we now have, in the X-ray spectrometric method of crystal analysis due to Sir William Bragg, a method of obtaining the exact absolute dimensions and volume of the unit cells of the space-lattice, from the spacings of the parallel planes of atoms which are parallel to the three axial planes, and Sir William Bragg kindly undertook to determine these, for the sulphates of potassium, rubidium, caesium, and ammonium, with the same crystals as had been used by the author in his research. The work was carried out in 1916, in Sir William Bragg's laboratory, by Prof. Ogg and Mr. F. L. Hopwood, and the results are given in the next table:—

Table of Cell-Dimensions.

Salt.	Length of Sides of Unit Rhomb.			Volume of Unit Rhomb.
	a.	b.	c.	
	cm.	cm.	cm.	c.c.
K_2SO_4 .	5.731×10^{-8}	10.008×10^{-8}	7.424×10^{-8}	425.78×10^{-24}
Rb_2SO_4 .	5.949×10^{-8}	10.394×10^{-8}	7.780×10^{-8}	481.14×10^{-24}
$(\text{NH}_4)_2\text{SO}_4$.	5.951×10^{-8}	10.560×10^{-8}	7.729×10^{-8}	485.71×10^{-24}
Cs_2SO_4 .	6.218×10^{-8}	10.884×10^{-8}	8.198×10^{-8}	554.88×10^{-24}

It will be seen that the absolute lengths of the cell-edges correspond almost exactly to the figures given in the second set of ratios in the previous table. Indeed, if those relative measures of the author have 10^{-7} cm. affixed to them they express the absolute dimensions in space. When it is remembered that these topic axial ratios were published as long ago as 1894 (in the cases of the alkali-metal salts), it is extremely satisfactory in these later days

to get their perfect confirmation as relative measures and their conversion to absolute ones.

Passing now to *The Optical Properties*, the ability to prepare 60° -prisms out of small crystals, of such relative softness compared with natural mineral crystals, by means of the cutting-and-grinding goniometer, confers the boon of being able to determine two of the three refractive indices with each prism. The crystals of the alkali sulphates being orthorhombic, there are no extinction directions to determine by means of the stauroscope, the three principal planes of the optical tri-axial ellipsoid being coincident with the three rectangular axial planes; and the three principal axes of the ellipsoid, the intersection directions of the three planes, are identical in direction with the crystal axes. It is the three refractive indices α , β , γ , corresponding to light vibrations parallel to these three axes, that have to be determined, and as the plane-surface-preparing goniometer just referred to enables a 60° -prism to be readily prepared with the most desirable orientation, so that its refracting edge shall be parallel to one of the three axes, and its bisecting plane parallel to a principal plane and also to a second axis, the two indices corresponding to these two axes are immediately afforded by such a prism when adjusted for minimum deviation on the spectrometer-goniometer, the excellent No. 1A Fuess instrument being used. The directions of vibration of the two images of the signal-slit, polarised at right angles to each other, then afforded are readily determined by means of the Nicol prism carried in front of the telescope eyepiece. The spectroscopic monochromatic illuminator enabled these images to be produced for a series of different wave-lengths of light distributed throughout the whole spectrum. The following table gives the three indices for six wave-lengths, for the five salts of the group, and the small table following it gives the mean indices, $1/3 (\alpha + \beta + \gamma)_{Na}$:—

Table of Refractive Indices.

Crystal axis.	Light.	K ₂ SO ₄ .	Rb ₂ SO ₄ .	Am ₂ SO ₄ .	Cs ₂ SO ₄ .	Tl ₂ SO ₄ .
<i>a</i>	Li . . .	1.4924	1.5120	1.5297	1.5633	1.8739
	C . . .	1.4928	1.5124	1.5302	1.5637	1.8755
	Na . . .	1.4947	1.5144	1.5330	1.5662	1.8853
	Tl . . .	1.4967	1.5166	1.5359	1.5690	1.8964
	F . . .	1.4995	1.5194	1.5394	1.5725	1.9126
	G . . .	1.5024	1.5235	1.5445	1.5775	—
<i>b</i>	Li . . .	1.4912	1.5108	1.5199	1.5615	1.8563
	C . . .	1.4916	1.5112	1.5204	1.5619	1.8579
	Na . . .	1.4935	1.5131	1.5230	1.5644	1.8671
	Tl . . .	1.4955	1.5153	1.5258	1.5672	1.8778
	F . . .	1.4982	1.5181	1.5291	1.5706	1.8935
	G . . .	1.5012	1.5222	1.5340	1.5756	—
<i>c</i>	Li . . .	1.4950	1.5109	1.5177	1.5569	1.8493
	C . . .	1.4954	1.5113	1.5182	1.5573	1.8509
	Na . . .	1.4973	1.5133	1.5209	1.5598	1.8600
	Tl . . .	1.4994	1.5155	1.5237	1.5624	1.8704
	F . . .	1.5023	1.5183	1.5270	1.5660	1.8859
	G . . .	1.5052	1.5224	1.5318	1.5705	—

Mean Refractive Indices.

K ₂ SO ₄	1.4952
Rb ₂ SO ₄	1.5136
(NH ₄) ₂ SO ₄	1.5256
Cs ₂ SO ₄	1.5635
Tl ₂ SO ₄	1.8708

The *Refractive Indices* of rubidium sulphate are thus seen to be intermediate between those of potassium and caesium sulphates, this optical property thus showing the same progression with atomic number of metal as do the morphological constants already described.

Ammonium sulphate has refractive indices close to those of the rubidium salt. But thallium sulphate is distinguished by far greater refractive power, which will be shown later to be characteristic of thallium salts.

An interesting way of expressing this progressive change of refractive power, as potassium is replaced by rubidium and the latter in turn by caesium, is to construct the optical ellipsoids of the three salts from a common centre. We

can use either the Fresnel optical velocity ellipsoid or the index ellipsoid of MacCullagh, which latter is the polar reciprocal of Fresnel's ellipsoid, and is identical with the Indicatrix ellipsoid of Fletcher (the late Sir Lazarus), its *radii vectores* being proportional to the refractive indices themselves. The following table gives the principal-axial lengths, inversely proportional to the refractive indices, of the Fresnel ellipsoid, for the five salts of the group. The value along the *b*-axis of the potassium salt is taken as unity for all five, so that the progressive change on passing from one salt to another is indicated.

Axial Ratios of Optical Velocity Ellipsoids.

K ₂ SO ₄	0.9992 : 1	: 0.9975
Rb ₂ SO ₄	0.9862 : 0.9871	: 0.9869
(NH ₄) ₂ SO ₄	0.9742 : 0.9806	: 0.9820
Cs ₂ SO ₄	0.9536 : 0.9547	: 0.9575
Tl ₂ SO ₄	0.7922 : 0.7999	: 0.8030

It will be seen that the Fresnel ellipsoid of the rubidium salt lies inside that of the potassium salt, and that of the cæsium salt within that of the rubidium salt, so that the latter lies intermediately. If the indicatrices were compared the latter fact would still be true, but the cæsium salt ellipsoid would then be the outermost, and the potassium one the innermost. The axial directions are the same for all five, the symmetry being orthorhombic.

We ought next to compare the Lorenzian or Gladstonian constants, the *Molecular Refraction*, the values for which were all worked out from the formulæ $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$ (Lorenz) and $\frac{n - 1}{d} M$ (Gladstone), where *n* is the refractive index,

M the molecular weight, and *d* the density, so that $\frac{M}{d} = V$, the molecular volume. Taking the Gladstonian results as typical, for both show the same relationships, the molecular refractions are set down in the next table. The

last column, in which the mean of all three values for the three axial directions is given, affords a particularly clear comparison.

Table of Molecular Refractions

	Gladstone, $\frac{n-1}{d}$ M.			Mean. $\frac{1}{3}(\alpha + \beta + \gamma)$.
	Axis a.	Axis b.	Axis c.	
K ₂ SO ₄ . . .	32.01	31.94	32.18	32.04
Rb ₂ SO ₄ . . .	37.61	37.52	37.53	37.55
(NH ₄) ₂ SO ₄ . . .	39.29	38.56	38.40	38.75
Cs ₂ SO ₄ . . .	47.71	47.56	47.17	47.48
Tl ₂ SO ₄ . . .	64.74	63.47	62.95	63.72

Again it is seen that rubidium sulphate stands intermediate between potassium and caesium sulphates as regards molecular refraction. The ammonium salt stands close to the rubidium salt, as for so many other properties. But the thallium salt again distinguishes itself by very high molecular refraction.

A particularly interesting result was afforded by a comparison which was made between the refraction equivalents for the crystals and those for the state of solution of the salts in water, a number of determinations of which were made with the greatest care, involving determinations of the refractive indices and the densities of some nearly saturated solutions. The results are given in the following table.

Table of Refraction Equivalents for Solid and Solution.

	Crystals.	Solution.	Difference.
K ₂ SO ₄ . . .	32.25	33.39	+1.14
Rb ₂ SO ₄ . . .	37.77	38.39	+0.62
(NH ₄) ₂ SO ₄ . . .	39.06	39.67	+0.61
Cs ₂ SO ₄ . . .	47.81	47.57	-0.24

It will be observed that the change of state, from the

crystallised solid to that of solution in water, causes a slight change in molecular refraction, and that the differences for the three alkali metallic salts are progressive, a positive difference of just over a unit for the potassium salt, a smaller positive difference for the rubidium salt, and a very small negative difference for the cæsium salt, rubidium sulphate once more proving itself intermediate. The ammonium salt, moreover, shows a difference practically identical with that of the rubidium salt. This beautiful result shows that the progression according to atomic number and weight of the alkali metal extends to the minutest details of the physical properties.

Finally, as regards the *Optic Axial Angles* and the general nature of the interference phenomena in convergent polarised light, some extraordinary phenomena were observed, all having their root in the principle which has been found to apply both to this rhombic series of salts and to the monoclinic double salts, namely, that the double refraction (best measured by the difference between the extreme refractive indices α and γ) diminishes as atomic weight and atomic number of the alkali metal increases.

In the case of the sulphates the double refraction is already very small in the initial potassium salt, as shown in the curve diagram, Fig. 40, in which atomic weight is taken for ordinates and the length of the Fresnel ellipsoid-axes (representing inversely the refractive indices) as abscissæ.

The thick continuous curves give the conditions for each salt separately, b -axis = 1 in each salt; the dotted ones take the b of potassium sulphate as 1 for all three salts, and thus show the progress from salt to salt. Considering first the ellipsoid-axes which correspond in direction to the crystal axes a and b , they are close together for all three salts, to about the same (parallel) extent. But the c -value, not far from the a -value in the potassium salt, alters very rapidly when that metal is replaced by rubidium,

having actually crossed a and nearly reached b . On reaching the caesium salt the c -value has got far beyond the b -value, and the sign of the double refraction is reversed, from positive to negative. But the most interesting result is the remarkable condition of things in the rubidium salt, for not only are the but slightly differing a - and b -values now the two extremes, marking a great reduction of double

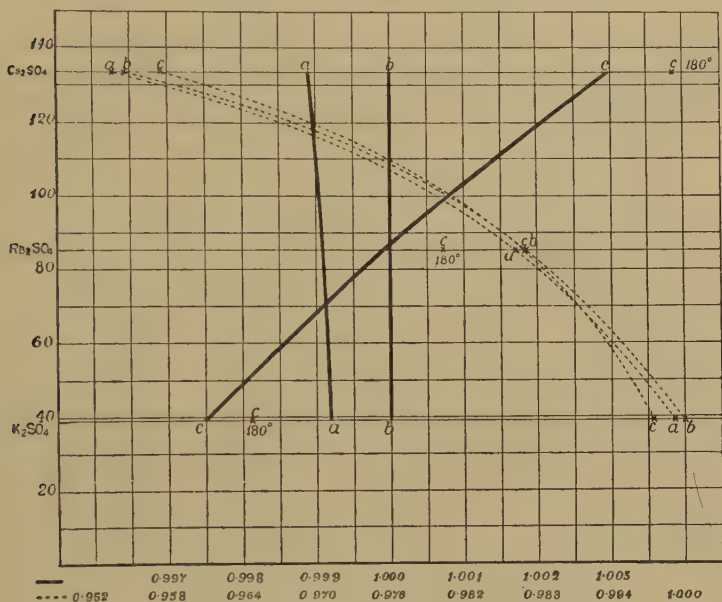


FIG. 40.—Curve of Double Refraction Conditions.

refraction, but the c - and b -values are so very close together that the corresponding indices of refraction for sodium light only differ by two units in the fourth place of decimals, being 1.5133 and 1.5131. The signal-images afforded by the 60° -prism used to determine these two refractive indices β and α actually overlap. The other index, γ , is also unusually near, namely, 1.5144, only 0.0011 from β .

Now these are just the ideal conditions for the display of crossed-axial-plane dispersion of the optic axes. Potassium and caesium sulphates are found to behave normally

as low doubly refractive crystals, of positive and negative character respectively however, owing to the reversal mentioned as the result of the rapid change of the c -value. But rubidium sulphate gives no interference figure in convergent polarised light with section-plates even somewhat thicker than those affording good figures with the other two salts, but only broad spectrum bands or curves; and it is only when a section-plate or rather block nearly a centimetre thick is prepared, perpendicular to the acute bisectrix of the optic axial angle, that a clear interference figure is obtained. This figure, however, is not the usual one, but a very beautiful one resembling that afforded by brookite, titanium dioxide TiO_2 , which is one of the best known examples of a substance showing crossed-axial-plane dispersion, the optic axes being separated widely in one plane for red light and in the perpendicular plane also widely, for blue light. At the ordinary temperature, however, crossing is not actually attained in the case of rubidium sulphate, but there is a difference of over thirty degrees in the angle for red and for blue light, that for the former being very small, a near approach to a uniaxial figure.

On warming the section-block, however, the optic-axial brushes approach and coalesce in the centre almost at once, forming the uniaxial rectangular black cross and circular rings, for each wave-length in turn at a specific temperature, thus, for instance, at 36°C . for red lithium light, for sodium yellow light at 38° , and so on, the cross opening out again as the temperature slowly rises and the brushes separating in the vertical plane, having previously been separated in the horizontal plane. Even for violet light (G) the uniaxial figure was formed at 60° , the axes being then separated in the vertical plane by no less than 60° for red lithium light. Fig. 49 on page 123 will assist in following this description.

These observations indicated that if the 60° -prism were

warmed, which afforded the α and β refractive indices, the signal-images, already overlapping considerably, should for each wave-length of light in turn come into more complete coincidence and then cross and pass each other on the other side, the right becoming the left image and *vice versa*. The experiment, on being tried, succeeded exactly as expected. Indeed it may be here stated that all the refractive index and optic axial phenomena throughout the research were repeated at higher temperatures, after completion of the ordinary temperature measurements, to assure oneself that the conclusions drawn were independent of temperature and not merely derived from a fortuitous occurrence at the ordinary temperature.

These beautiful phenomena with rubidium sulphate are entirely caused by the progressive diminution of the double refraction with the atomic number and weight of the alkali metal, causing a complete reversal of sign from a small positive double refraction in the potassium salt, through a very minute positive amount with a consequently delicate balance in the rubidium salt, to a small negative double refraction in the cæsium salt, as one alkali metal is replaced by another of higher atomic number and weight. That is, the at first almost incomprehensible optical properties of rubidium sulphate proved to be the direct result of the law of progression with atomic number and weight.

The Rhombic Selenates.—The results which have now been described for the rhombic alkali sulphates are very closely paralleled by the corresponding selenates of potassium, rubidium, and cæsium, and precisely the same conclusions are derived from them, the progression according to atomic number and weight being equally clear. The absolute values of all the constants are different, pushed along somewhat as it were by the replacement of sulphur by selenium, which two elements belong exclusively to the same family Group VI and to odd series, 3 and 5, so that appreciable differences even in crystal angles are apparent,

just as when the alkali metals are interchanged. But the relationships between the three salts are almost identical with those for the three sulphates.

As regards the last property dealt with, the optic-axial interference phenomena in convergent polarised light, the same remarkable effect of progressive diminution of the double refraction, causing crossing of the optic-axial planes for different wave-lengths of light at specific temperatures, is observed. But in this selenate group it occurs for the cæsium salt, the diminution reaching its critical stage later in the group. Indeed cæsium selenate is the more remarkable, for within a range of 280° of temperature the acute bisectrix of the optic axial angle becomes parallel to all three of the crystal-axes (and the axes of the ellipsoid identical therewith) in turn, first at the ordinary temperature with b , then with a , and finally with c . Moreover, the plane of the optic axes crosses from c (001) to b (010), the crossing at 95° being accompanied by temporary uniaxial properties, with rectangular cross and circular interference rings, as in the case of rubidium sulphate. Further, the sign of the double refraction changes first from negative to positive, and then back again to negative.

For when the plate perpendicular to the axis b , the acute bisectrix of the optic axial angle, is heated, the first effect is to cause the optic brushes to separate still further, till they disappear out of the field; following them with another plate perpendicular to axis a they approach each other as the plate is heated beyond the temperature which the first plate had reached, and come to coincidence in the centre at temperatures ranging from 92° to 98° for the different wave-lengths of light, with production of the uniaxial cross and rings. Beyond this they reopen, but in the vertical plane (the other having been the horizontal), and eventually move off the field at the top and bottom ends of the vertical diameter. Still following with a third plate

perpendicular to axis c , the axial brushes appear when the temperature has passed what had formerly been attained, and at 280° , when the heating had to be stopped in order to save the very valuable polariscope from injury, they were again approaching the centre.

All these section-plates, or really blocks, had to be a centimetre thick, in order to get well-defined interference figures, the double refraction being so small. Correspondingly, the 60° -prism affording the α and β refractive index images, shows the latter to coalesce at 95° , and then to pass each other on the opposite side, as β and α .

The whole of these unique optical phenomena are the direct consequence of the progressive change in the nature of the optical ellipsoid, both at the ordinary temperature and on raising the latter, which accompanies the progressive change in atomic number and weight.

There is one remarkable difference in the case of the selenate group, of which so far only the three alkali metallic salts have been referred to, and which are strictly parallel in all respects to the sulphates. It occurs in the case of ammonium selenate; for when this salt is prepared by passing ammonia gas into selenic acid, the crystals deposited are monoclinic, quite different to the rhombic crystals of ammonium sulphate. But if a solution be made of equal molecular proportions of ammonium sulphate and ammonium selenate, the mixed solution deposits rhombic crystals like those of ammonium sulphate. If two molecular proportions of the selenate are used, to one of sulphate, both rhombic and monoclinic crystals are deposited. But if solutions containing one molecular proportion of rubidium selenate and either one or two molecular proportions of ammonium selenate are made, rhombic crystals only are produced on cooling and evaporation. In the last-mentioned case, moreover, the crystals contained, in the particular experiments made, over sixty per cent. of ammonium selenate. The ease with which

these two last mentioned salts crystallise together is due to the very close similarity, almost identity, of the dimensions of their space-lattice cells, as has already been pointed out in the cases of ammonium and rubidium sulphates.

In 1862 the late Prof. von Lang described some rhombic crystals of ammonium selenate, and 44 years afterwards most kindly presented them to the author, who found that they contained a considerable amount of the sulphate, being, in fact, mixed crystals. Some small crystals of the monoclinic variety, for it is obvious that ammonium selenate is dimorphous, were also found by the author mixed among the rhombic ones, and these had escaped notice hitherto.

In spite of the fact that the pure rhombic form could not be isolated, the physical properties even of the monoclinic form followed the rule of similarity to those of the rubidium salt.

Thermal Expansion of the Rhombic Sulphates.—The three sulphates of the alkali metals, being anhydrous salts (without any water of crystallisation), are particularly suitable for determinations of the coefficients of expansion by heat, by the author's interferometric method described in Chapter III, provided blocks of the crystals at least a centimetre thick can be obtained. After many and prolonged fruitless attempts homogeneous crystals of all three salts of adequate size were eventually obtained. A pair of parallel surfaces about a centimetre apart, and perpendicular to a crystal axis, were ground and polished on each of the crystals selected, and these blocks were used for the determination of the thermal expansion along that axis. For the three crystallographic axes of an orthorhombic crystal are identical in direction with the axes of the thermal ellipsoid. Six to eight determinations were made with separate crystals for each axis of each salt, altogether 64 determinations having been made. Each occupied five to seven hours, the movement of the inter-

ference bands having been watched throughout, for two intervals of temperature, the first up to about 60° and the second from that temperature up to about 100° C., as described in Chapter III. The method of mounting the crystal on the platinum-iridium tripod was that shown in Fig. 24 (page 66).

The results for the linear expansions along the three crystal axes of potassium sulphate are given below, as typical of the kind of result obtained with all three salts, and also that for the cubical expansion, which is the sum of the a and b constants of the three linear expansions, as other terms obtained by taking the product do not affect the last significant place of decimals.

Linear expansion along axis	Constant a .			Constant b .			
a	0.000	036	16	0.000	000	014	4
b	0.000	032	25	0.000	000	014	1
c	0.000	036	34	0.000	000	041	3
Cubical expansion of K_2SO_4 .	0.000	104	75	0.000	000	069	8

The mean coefficient of expansion between the temperatures 0° and t° is $a + bt$. That for any temperature t , or the mean coefficient between any two temperatures whose mean is t , is $a + 2bt$. Below are given the cubical coefficients of expansion $a + 2bt$ for all three salts.

$$K_2SO_4 \quad 0.000 \ 104 \ 75 + 0.000 \ 000 \ 139 \ 6t$$

$$Rb_2SO_4 \quad 0.000 \ 103 \ 14 + 0.000 \ 000 \ 153 \ 4t$$

$$Cs_2SO_4 \quad 0.000 \ 101 \ 70 + 0.000 \ 000 \ 162 \ 0t$$

These values for the coefficient of cubical expansion show the progression of both constants with atomic number and weight of the alkali metal, in common with all the other properties of these salts which have been investigated. This work on the thermal dilatation of the sulphates was the most arduous and fatiguing which the author ever experienced; the fact of having to keep an eye on the

interference bands for at least five hours, without leaving the instrument, and for 64 such séances, will explain the reason. But the results were very repaying, and the magnificent performance of the interference dilatometer was most gratifying.

CHAPTER V

THE RESEARCH ON THE HEXAHYDRATED DOUBLE SULPHATES AND SELENATES

THE salts of the series $R_2M(S[Se]O_4)_2 \cdot 6H_2O$ crystallise, magnificently as regards all but a very few members, in the holohedral class 5 of the monoclinic system. The main reason for being attracted to them, as favourable subjects for this research, was that they comprise eight groups of double sulphates, and the same of double selenates, formed by the eight dyad-acting interchangeable M-metals, magnesium, zinc, iron, manganese, nickel, cobalt, copper, and cadmium; and that each of these groups, containing the same M-metal, comprise the five salts in which R is respectively potassium, rubidium, caesium, ammonium, and thallium. Hence they afforded sixteen times over the possibility of studying the effect of replacing one R-metal by another, and of observing whether the interesting relationships exhibited by the simple alkali sulphates still held, or were modified or negatived by these double salts. Also the symmetry being lower, monoclinic instead of rhombic, interfacial angular differences might be expected to be greater than in the more symmetric rhombic series of sulphates and selenates.

If all the salts were capable of existence there should be eighty (sixteen times five) of them. As a matter of fact only 64 have been successfully prepared in good crystals and studied. For the two potassium-manganese and two potassium-cadmium sulphates and selenates appear to be incapable of existence, and of the 16 possible thallium salts only four have been obtained in crystals adequately

perfect for such a research. But 64 is a large number for so thorough an investigation, and it has taken thirty years to complete the work. During this same time, however, the ten simple sulphates and selenates have also been studied and fully described, as related in the last chapter, and also (with Miss Mary Porter) the double chromates of ammonium, rubidium and cæsium, isomorphous with the double sulphate-selenate series, have been worked out. Hence 77 salts have been dealt with fully in this time. Moreover, all the various new instruments devised and constructed for the work have been described and illustrated.

An interesting light has been thrown on the probable reason why the four K . Mn and K . Cd salts are missing, by the fact that great difficulty, eventually overcome, was found in obtaining the potassium-ferrous selenate. This was partly due to the difficulty of first preparing ferrous selenate. Messrs. Merck, who offered to supply the required quantity, soon found themselves unable to do so, apparently quite unexpectedly. For ferrous selenate is not obtainable by the action of selenic acid on iron, as the action is so very slow that ferric oxidation occurs, and any nascent hydrogen liberated immediately reduces the selenic acid to the element selenium, a red deposit. After many experiments the author eventually discovered a satisfactory method in the action of selenic acid on ferrous sulphide. The action proceeds steadily and rapidly in the cold, and affords a ferrous product by reason of the sulphuretted hydrogen liberated preventing, by its reducing property, the oxidation of the ferrous iron to ferric.

Having obtained ferrous selenate satisfactorily, it might have been expected that by mixing its solution in correct molecular proportion with potassium selenate solution the double selenate would at once be obtained. But for long this double salt defied all attempts at preparation. Eventually, however, during a severe cold spell of weather

in the winter of 1918 four crops of excellent crystals were obtained, during the four coldest nights. But they only remained clear and undecomposed for four to six hours, becoming then opaque like porcelain and crumbling to decomposed powder. Hence, rapid and concentrated work on a clear previously arranged plan was necessary, in order to complete their investigation, which was eventually successfully achieved. It was clearly demonstrated that the salt is very unstable at the ordinary temperature, because its upper temperature-limit for existence is only 2° to 3° C. Hence, it is a reasonable conclusion that the potassium-manganese, and potassium-cadmium salts do not exist because their life-temperature limit would be below the freezing point of water.

It may also be mentioned here that the author has ventured to predict the probable crystal-elements, specific gravity, and refractive indices of these missing K . Mn and K . Cd salts, from the rules which have been found to apply generally throughout the series, as regards the relationships of analogous potassium, rubidium, and caesium salts.

As regards the results of the research it may be said at once that full confirmation has been obtained, and indeed with added emphasis, from every one of the sixteen groups, double selenates as clearly as double sulphates, and also from the double chromate group, of the law of progression according to atomic number or weight of the alkali metal. Also some additional facts of special interest have been observed, owing to the greater freedom offered by the lower degree of symmetry; the optical ellipsoid, for instance, being now capable of movement on replacement of one alkali metal by another, and not rigidly fixed to the position in which its axes are (as in the rhombic salts) coincident with the crystal-axes, shows a progressive rotation, following the change in atomic number of the alkali metal.

It will suffice to take any one group as typical of the sixteen. Taking the nickel double sulphate group, for

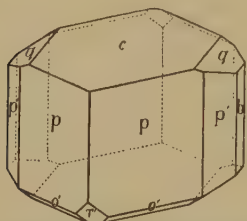


FIG. 41.—KNi Sulphate.

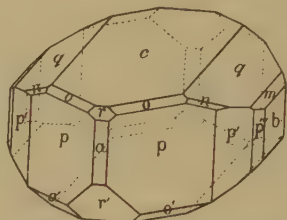


FIG. 42.—RbNi Sulphate.

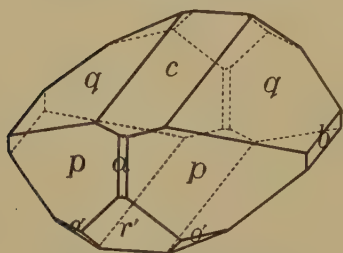


FIG. 43.—CsNi Sulphate.

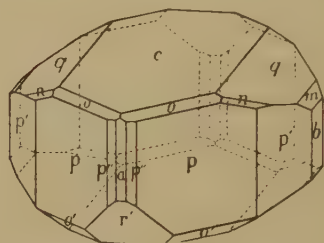


FIG. 44.—AmNi Sulphate.

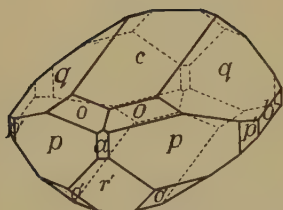


FIG. 45.—TiNi Sulphate.

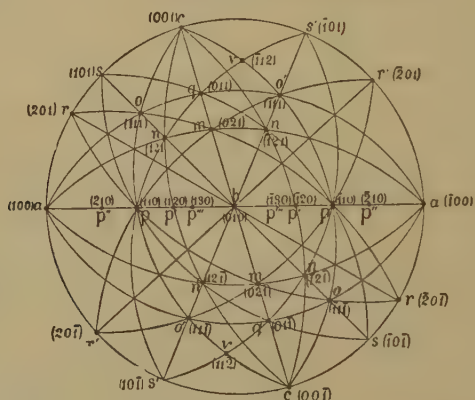


FIG. 46.—Stereographic Projection of Double Sulphates and Selenates.

which all five members have been obtained in excellent crystals, of a brilliant green colour, five typical crystals are shown in the above figures, together with the stereographic projection for the whole series.

The Crystal-Habit.—One of the most interesting special features of the double salt series is here shown very clearly as regards the potassium, rubidium, and caesium salts of the nickel group, which, however, is quite typical of every group. It concerns the “Habit” of the crystals, the relative development of the various faces, a most curious and distinct progression in habit being exhibited. All the crops of crystals of the potassium salts have shown a large preponderance of development of the basal pinakoid $c\{001\}$, as compared with a relatively much smaller development of the faces of the clino-domal prism $q\{011\}$, and also in the prism faces $p\{110\}$, the latter conferring a stout prismatic habit, that is, parallel to the vertical axis c . On the other hand the caesium salts have shown the reverse, markedly broad development of the $q\{011\}$ faces and only narrow $c\{001\}$ faces, and usually with the faces elongated backwards, conferring a prismatic habit parallel to the inclined axis a (front to back), the faces of the primary prism $p\{110\}$ being only moderately developed. A caesium salt crystal has never been observed of the first type, nor a potassium one of the second type. But the rubidium salt is distinguished by the more or less equal development of the $c\{001\}$ and $q\{011\}$ faces, at any rate these latter faces are always well developed, the c -faces fairly broad, and the $p\{110\}$ faces prominent. Thus the crystals of the rubidium salt are of a distinctly intermediate type between those of the potassium and caesium salts. The ammonium and thallium salts show every variety of habit which has been mentioned, but a preponderance of crystals of the ammonium salt more closely approximate to the rubidium salt type than to any other.

The Crystal-Elements and Angles.—Next follow two tables of angles and axial ratios of the five salts of the nickel group, and a third table showing the average and maximum differences in interfacial angle from the potassium salt.

Nickel Group of Double Sulphates.

Table of Interfacial Angles.

Angle.	KNi sulphate.	RbNi sulphate.	CsNi sulphate.	AmNi sulphate.	TiNi sulphate.
$\left\{ \begin{array}{l} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \\ cr' = (001) : (\bar{2}01) \\ cs' = (001) : (\bar{1}01) \\ s'r' = (\bar{1}01) : (\bar{2}01) \\ r'a = (\bar{2}01) : (\bar{1}00) \end{array} \right.$	$\begin{array}{l} 75^\circ \ 0' \\ 45 \ 48 \\ 29 \ 12 \\ 63 \ 44 \\ 38 \ 33 \\ 25 \ 11 \\ 41 \ 16 \end{array}$	$\begin{array}{l} 73^\circ \ 57' \\ 45 \ 4 \\ 28 \ 53 \\ 64 \ 36 \\ 38 \ 57 \\ 25 \ 39 \\ 41 \ 27 \end{array}$	$\begin{array}{l} 72^\circ \ 58' \\ 44 \ 21 \\ 28 \ 37 \\ 65 \ 28 \\ 39 \ 22 \\ 26 \ 6 \\ 41 \ 34 \end{array}$	$\begin{array}{l} 73^\circ \ 3' \\ 44 \ 35 \\ 28 \ 28 \\ 65 \ 5 \\ 39 \ 1 \\ 26 \ 4 \\ 41 \ 52 \end{array}$	$\begin{array}{l} 73^\circ \ 36' \\ 45 \ 3 \\ 28 \ 33 \\ 64 \ 27 \\ 38 \ 39 \\ 25 \ 48 \\ 41 \ 57 \end{array}$
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \\ pb = (110) : (010) \end{array} \right.$	$\begin{array}{l} 35 \ 29 \\ 19 \ 28 \\ 35 \ 3 \\ 54 \ 31 \end{array}$	$\begin{array}{l} 35 \ 17 \\ 19 \ 28 \\ 35 \ 15 \\ 54 \ 43 \end{array}$	$\begin{array}{l} 34 \ 48 \\ 19 \ 28 \\ 35 \ 44 \\ 55 \ 12 \end{array}$	$\begin{array}{l} 35 \ 11 \\ 19 \ 28 \\ 35 \ 21 \\ 54 \ 49 \end{array}$	$\begin{array}{l} 35 \ 24 \\ 19 \ 28 \\ 35 \ 8 \\ 54 \ 36 \end{array}$
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \end{array} \right.$	$\begin{array}{l} 25 \ 52 \\ 64 \ 8 \end{array}$	$\begin{array}{l} 25 \ 44 \\ 64 \ 16 \end{array}$	$\begin{array}{l} 25 \ 28 \\ 64 \ 32 \end{array}$	$\begin{array}{l} 25 \ 34 \\ 64 \ 26 \end{array}$	$\begin{array}{l} 25 \ 37 \\ 64 \ 23 \end{array}$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oj = (111) : (011) \\ aq = (100) : (011) \\ qo' = (011) : (\bar{1}11) \\ o'u = (\bar{1}11) : (\bar{1}00) \end{array} \right.$	$\begin{array}{l} 48 \ 59 \\ 27 \ 33 \\ 76 \ 32 \\ 34 \ 46 \\ 68 \ 42 \end{array}$	$\begin{array}{l} 48 \ 16 \\ 27 \ 19 \\ 75 \ 35 \\ 35 \ 5 \\ 69 \ 20 \end{array}$	$\begin{array}{l} 47 \ 32 \\ 27 \ 8 \\ 74 \ 40 \\ 35 \ 31 \\ 69 \ 49 \end{array}$	$\begin{array}{l} 47 \ 46 \\ 26 \ 59 \\ 74 \ 45 \\ 35 \ 8 \\ 70 \ 7 \end{array}$	$\begin{array}{l} 48 \ 14 \\ 27 \ 1 \\ 75 \ 15 \\ 34 \ 51 \\ 69 \ 54 \end{array}$
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (\bar{1}11) \\ o'c = (\bar{1}11) : (00\bar{1}) \end{array} \right.$	$\begin{array}{l} 34 \ 46 \\ 43 \ 4 \\ 77 \ 50 \\ 57 \ 26 \\ 44 \ 44 \end{array}$	$\begin{array}{l} 34 \ 25 \\ 42 \ 32 \\ 76 \ 57 \\ 57 \ 57 \\ 45 \ 6 \end{array}$	$\begin{array}{l} 34 \ 0 \\ 42 \ 5 \\ 76 \ 5 \\ 58 \ 31 \\ 45 \ 24 \end{array}$	$\begin{array}{l} 33 \ 58 \\ 42 \ 15 \\ 76 \ 13 \\ 58 \ 39 \\ 45 \ 8 \end{array}$	$\begin{array}{l} 34 \ 6 \\ 42 \ 36 \\ 76 \ 42 \\ 58 \ 26 \\ 44 \ 52 \end{array}$
$\left\{ \begin{array}{l} bo = (010) : (111) \\ os = (111) : (101) \end{array} \right.$	$\begin{array}{l} 70 \ 12 \\ 19 \ 48 \end{array}$	$\begin{array}{l} 70 \ 25 \\ 19 \ 35 \end{array}$	$\begin{array}{l} 70 \ 48 \\ 19 \ 12 \end{array}$	$\begin{array}{l} 70 \ 40 \\ 19 \ 20 \end{array}$	$\begin{array}{l} 70 \ 31 \\ 19 \ 29 \end{array}$
$\left\{ \begin{array}{l} bo' = (010) : (\bar{1}11) \\ o's' = (\bar{1}11) : (\bar{1}01) \end{array} \right.$	$\begin{array}{l} 65 \ 17 \\ 24 \ 43 \end{array}$	$\begin{array}{l} 65 \ 11 \\ 24 \ 49 \end{array}$	$\begin{array}{l} 65 \ 15 \\ 24 \ 45 \end{array}$	$\begin{array}{l} 65 \ 8 \\ 24 \ 52 \end{array}$	$\begin{array}{l} 65 \ 11 \\ 24 \ 49 \end{array}$
$\left\{ \begin{array}{l} sq = (101) : (011) \\ qp = (011) : (\bar{1}10) \\ ps = (\bar{1}10) : (\bar{1}0\bar{1}) \end{array} \right.$	$\begin{array}{l} 38 \ 13 \\ 86 \ 22 \\ 55 \ 25 \end{array}$	$\begin{array}{l} 37 \ 56 \\ 87 \ 17 \\ 54 \ 47 \end{array}$	$\begin{array}{l} 37 \ 35 \\ 88 \ 23 \\ 54 \ 2 \end{array}$	$\begin{array}{l} 37 \ 32 \\ 88 \ 4 \\ 54 \ 24 \end{array}$	$\begin{array}{l} 37 \ 37 \\ 87 \ 32 \\ 54 \ 51 \end{array}$
$\left\{ \begin{array}{l} s'q = (\bar{1}01) : (011) \\ qp = (011) : (110) \\ ps' = (110) : (10\bar{1}) \end{array} \right.$	$\begin{array}{l} 45 \ 17 \\ 63 \ 43 \\ 71 \ 0 \end{array}$	$\begin{array}{l} 45 \ 32 \\ 63 \ 0 \\ 71 \ 28 \end{array}$	$\begin{array}{l} 45 \ 44 \\ 62 \ 27 \\ 71 \ 49 \end{array}$	$\begin{array}{l} 45 \ 30 \\ 62 \ 23 \\ 72 \ 7 \end{array}$	$\begin{array}{l} 45 \ 14 \\ 62 \ 45 \\ 72 \ 1 \end{array}$
$\left\{ \begin{array}{l} r'o' = (\bar{2}01) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pr' = (110) : (20\bar{1}) \end{array} \right.$	$\begin{array}{l} 34 \ 43 \\ 93 \ 1 \\ 52 \ 16 \end{array}$	$\begin{array}{l} 35 \ 6 \\ 92 \ 38 \\ 52 \ 16 \end{array}$	$\begin{array}{l} 35 \ 22 \\ 92 \ 32 \\ 52 \ 6 \end{array}$	$\begin{array}{l} 35 \ 25 \\ 92 \ 5 \\ 52 \ 30 \end{array}$	$\begin{array}{l} 35 \ 11 \\ 92 \ 8 \\ 52 \ 41 \end{array}$

Monoclinic Double Sulphates of the Nickel Group.

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β .	$a : b : c$
Potassium nickel sulphate . .	105° 0'	0·7379 : 1 : 0·5020
Rubidium nickel sulphate . .	106 3	0·7350 : 1 : 0·5022
Ammonium nickel sulphate . .	106 57	0·7373 : 1 : 0·5000
Cæsium nickel sulphate . .	107 2	0·7270 : 1 : 0·4984
Thallium nickel sulphate . .	106 23	0·7404 : 1 : 0·4997

Table of Average and Maximum Angular Changes.

Replacement.	Average change.	Maximum change.
K by Rb	27'	63' = 1° 3'
K by Cs	54	122 = 2 2
K by NH ₄	49	117 = 1 57
K by Tl	33	84 = 1 24

The symmetry being monoclinic, there is now another crystal element to record, besides the ratio of the crystal-axes, namely, the important axial angle β , the angle between the two axes a and c , which are inclined at an angle other than 90° in this system. The other axial angles, α and γ , are 90° . Hence the second table includes also the values of the axial angle β , as well as the axial ratios. From these tables the following facts will be obvious.

(1) The important monoclinic axial angle β increases equally by just a whole degree when potassium is replaced by rubidium or the latter by cæsium, the value of the angle for the rubidium salt being thus half-way between the values for the potassium and cæsium salts. That is, this angle varies directly as the atomic numbers and weights of the three interchangeable alkali metals. The values for the ammonium and thallium salts lie between those for the rubidium and cæsium salts, or very near to one of them.

That these relationships are not fortuitous ones for this particular group only, will be proved by now giving those

for the three other groups for which all five salts have been investigated.

				Axial angle.	Crystal axial ratios.
					$a : b : c$
KZn sulphate	.	.	.	104° 48'	0.7413 : 1 : 0.5044
RbZn "	.	.	.	105 53	0.7373 : 1 : 0.5011
CsZn "	.	.	.	107 1	0.7274 : 1 : 0.4960
AmZn "	.	.	.	106 52	0.7368 : 1 : 0.4997
TlZn "	.	.	.	106 16	0.7413 : 1 : 0.5010
KZn selenate	.	.	.	104 12	0.7458 : 1 : 0.5073
RbZn "	.	.	.	105 16	0.7431 : 1 : 0.5019
CsZn "	.	.	.	106 11	0.7314 : 1 : 0.4971
AmZn "	.	.	.	106 14	0.7409 : 1 : 0.5040
TlZn "	.	.	.	105 54	0.7479 : 1 : 0.5022
KCo sulphate	.	.	.	104 55	0.7404 : 1 : 0.5037
RbCo "	.	.	.	106 1	0.7391 : 1 : 0.5011
CsCo "	.	.	.	107 8	0.7270 : 1 : 0.4968
AmCo "	.	.	.	107 2	0.7386 : 1 : 0.4975
TlCo "	.	.	.	106 25	0.7413 : 1 : 0.4995

The above values for the potassium-zinc sulphate and selenate groups, and for the potassium-cobalt sulphate group, quite clearly bear out the statement of the angular relationships above given.

(2) The axial ratios, in all cases where the closeness does not become so extreme as to come within the range of experimental error, for the rubidium salt are intermediate between the corresponding ratios for the potassium and caesium salts. Those of the ammonium and thallium salts are obviously such as place these salts in the same isomorphous series as the alkali metallic salts, without showing any relationship to atomic number or weight.

(3) The average value of all the interfacial angular changes, and also the maximum change observed (that is, for the angle which changes most), for the replacement of potassium by caesium is practically exactly double that for the replacement of potassium by rubidium, corresponding to the doubling of the difference of the atomic numbers and weights. This is such an interesting result

that it is worth while giving a table showing all these average and maximum angular changes for the twelve groups in which all three alkali-metallic salts exist and have been studied.

Table of Average and Maximum Changes of Angle.

Group.	Average Change for Re- placement of K by				Maximum Change for Re- placement of K by			
	Rb.	Cs.	NH ₄ .	Tl.	Rb.	Cs.	NH ₄ .	Tl.
Mg sulphate .	29'	58'	56'		71'	141'	138'	
Zn „ .	26	56	50	35'	65	139	124	88'
Fe „ .	32	65	62		72	145	138	
Ni „ .	27	54	49	33	63	122	117	84
Co „ .	27	56	52	36	66	137	127	90
Cu „ .	22	47	39		53	115	101	
Mg selenate .	23	52	53		56	128	129	
Zn „ .	27	52	49	41	64	131	122	102
Fe „ .	27	55	54		69	139	139	
Ni „ .	23	47	45		57	119	110	
Co „ .	25	53	49		64	136	126	
Cu „ .	33	61	47		79	148	125	
Mean values .	27'	55'	50'	36'	65'	133'	125'	91'

At the bottom of the table the mean of the twelve sets of results is taken. The mean average changes for the two replacements, of potassium by rubidium, and the latter by cæsium, 27' and 55', stand wonderfully exactly as 1 to 2, and the mean maxima, 65' and 133', almost equally so. The average and maximum changes for the ammonium and thallium substitutions for potassium lie between those for the replacement of potassium by rubidium or cæsium, the thallium substitution giving rise to the lesser of the two amounts.

These interfacial angular changes are probably as large as will ever be observed, the symmetry, monoclinic, being low, while the interchangeable alkali metals are the most vigorous elements in chemical affinity and electro-positive character. The maximum amount observed was 2° 28',

between the potassium and cæsium salts of the copper-selenate group in the case of one of the angles.

The Volume Constants.—Considering next these constants, their values for the nickel group of double sulphates are appended, as a typical example of what occurs in all the groups.

Table of Volume Constants.

Salt.	Molecular volume.	Topic axial ratios.
		$\chi \quad : \quad \psi \quad : \quad \omega$
KNi sulphate	193.99	6.0170 : 8.1542 : 4.0934
RbNi " 	203.43	6.1065 : 8.3081 : 4.1723
NH ₄ Ni " 	203.91	6.1426 : 8.3312 : 4.1656
CsNi " 	215.90	6.2097 : 8.5416 : 4.2572
TiNi " 	201.97	6.1354 : 8.2865 : 4.1408

The molecular volumes and topic axial ratios, representing the relative volumes and edge-lengths of the parallelepipedal cells of the monoclinic space-lattice, for the rubidium salt are in every case intermediate between the corresponding volumes or edge-dimensions for the potassium and cæsium salts. The volume and edge-lengths for the ammonium salt are very close, especially the volume, to those of the rubidium salt of the group. Thus the rubidium and ammonium salts of the same group, in all the 17 groups dealt with, including the double chromate group, are wonderfully closely isostructural, just as was observed in the case of the simple rhombic salts. The thallium salt also comes near to the rubidium salt as regards these unit-cell constants.

Optics. Situation of the Optical Ellipsoid.—The crystals being monoclinic, a new possible variant appears, namely, the position of the optical ellipsoid and its axes, with reference to the crystal-axes. Only one of these crystal-axes, the symmetry axis *b*, is now identical with an axis of the ellipsoid, instead of all three being identical in

direction with the crystal-axes, as they are in the orthorhombic system. This power of movement when one alkali metal is replaced by another, or by ammonium or thallium, is actually exercised to a considerable extent, and in a progressive manner, following the order of the atomic number and weight of the alkali metal. The position of the ellipsoid for the potassium salt of any group, assuming it to be centred about the same point as the crystal-axes, is such that one of its principal axes is near to the vertical crystal-axis c , being rotated a very few degrees in front of

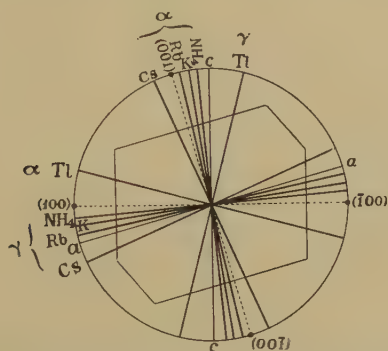


FIG. 47.—Extinction Directions of Nickel Group of Double Sulphates.

it. For the rubidium salt, the forward movement, rotation of the ellipsoid about the symmetry axis b , is several degrees more, and for the caesium salt the rotation is considerably more, the amount of rotation increasing with the atomic number of the alkali metal more than in mere simple proportion. The exact positions for a typical case, that of the nickel group of sulphates, are next given and illustrated in Fig. 47. The ammonium salt is included (in both table and figure), for which the position is always nearest of all these four salts to the c -axis. The thallium salt position, also given in the figure, always lies behind the vertical axis some considerable distance, in this group $13^{\circ} 29'$.

*Table of Positions of Optical Ellipsoid.**Inclinations of α extinctions of Ni salts in front of axis c.*

(2M.L. for Am, K, and Rb salts, 1M.L. for Cs salt.)

AmNi sulphate	5° 12'	RbNi sulphate	12° 38'
KNi	8° 42'	CsNi	24° 7'

In the figure, which is supposed to be a section parallel to the symmetry plane $b\{010\}$, the positions of the other rectangular axis of the ellipsoid lying in this plane are also given, and show, of course, the same progression. These two axes of the ellipsoid are the extinction directions determined by the stauroscope, a polariscope specially designed for the purpose, which enables the directions to be determined with respect to faces on the edge of the section-plate, which can be located first goniometrically, more accurately than with the polarising microscope. They are also the acute and obtuse bisectrices of the optic-axial-angle.

The beautiful way in which every detail of the crystal properties follows the progression of atomic number and weight of the alkali metal is strikingly illustrated by this rotation of the optical ellipsoid about the unique symmetry axis of the crystals, when potassium is replaced by rubidium and then the latter by cæsium. It can be charmingly imitated by a lantern slide model, in which the elliptic section of the ellipsoid can be rotated about the centre in its own plane, to the three positions one after the other, relatively to the outline of the crystal, representing a section parallel to the symmetry plane. Fig. 48 will assist in following the experiment.

The Refractive Indices.—The refractive indices for the nickel sulphate group are given in the next table, which also gives at the foot the mean refractive index $\frac{\alpha + \beta + \gamma}{3}$

for sodium light, and the amount of the double refraction $\gamma - \alpha$, also for sodium light as being a mid-spectrum wavelength.

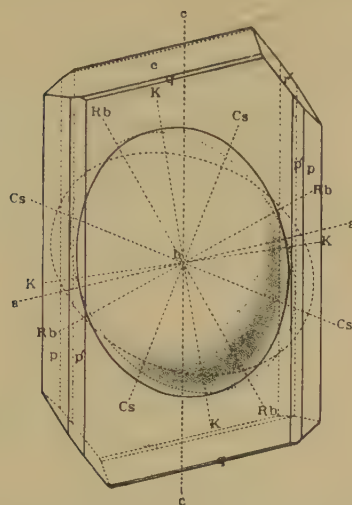


FIG. 48.—Experiment of Rotating Ellipsoid.

Progressive Rotation of Optical Ellipsoid on passing from a K Salt to a Rb Salt and thence to a Cs Salt, in Monoclinic Double Sulphates and Selenates.

The conclusions to be derived from the tables, not only for this group but for all the groups, are as follows :—

Table of Refractive Indices.

Index.	Light.	KNi sulphate.	RbNi sulphate.	NH ₄ Ni sulphate.	CsNi sulphate.	TiNi sulphate.
α	Li . . .	1.4809	1.4868	1.4916	1.5061	1.5984
	C . . .	1.4813	1.4872	1.4921	1.5065	1.5990
	Na . . .	1.4836	1.4895	1.4949	1.5087	1.6024
	Tl . . .	1.4860	1.4920	1.4976	1.5112	1.6063
	F . . .	1.4889	1.4949	1.5007	1.5146	1.6115
	G . . .	1.4933	1.4996	1.5060	1.5192	1.6191
β	Li . . .	1.4889	1.4933	1.4975	1.5100	1.6144
	C . . .	1.4893	1.4937	1.4980	1.5104	1.6150
	Na . . .	1.4916	1.4961	1.5007	1.5129	1.6183
	Tl . . .	1.4941	1.4987	1.5037	1.5154	1.6222
	F . . .	1.4972	1.5017	1.5069	1.5187	1.6280
	G . . .	1.5015	1.5062	1.5123	1.5235	1.6356
γ	Li . . .	1.5022	1.5023	1.5046	1.5133	1.6184
	C . . .	1.5026	1.5027	1.5051	1.5137	1.6190
	Na . . .	1.5051	1.5052	1.5081	1.5162	1.6224
	Tl . . .	1.5077	1.5078	1.5110	1.5189	1.6264
	F . . .	1.5109	1.5110	1.5142	1.5221	1.6324
	G . . .	1.5153	1.5156	1.5196	1.5266	1.6400
Mean refractive index $\frac{1}{3}(\alpha + \beta + \gamma)$ for Na light		1.4934	1.4969	1.5012	1.5126	1.6144
Double refraction, Na γ - α . . .		0.0215	0.0157	0.0132	0.0075	0.0200

The refractive indices of the rubidium salt are intermediate between those for the corresponding potassium and caesium salts, and nearer to the values for the potassium salt, the increase in refractive power becoming relatively greater as the atomic number of the alkali metal increases. The refractive indices of the ammonium salt lie between those of the analogous rubidium and caesium salts, but those of the thallium salt are far higher, the thallium salts investigated during the research having all distinguished themselves by relatively very great refractive power.

The *Double Refraction* diminishes considerably, and progressively with the atomic number and weight of the alkali metal, as potassium is replaced by rubidium, and the latter in turn by caesium.

This latter fact results in the caesium salt of any group exhibiting extremely low double refraction. In two of the groups, the magnesium sulphate and selenate groups, it leads, as it did on gently warming in the cases of rubidium sulphate and caesium selenate, to the display of crossed-axial-plane dispersion of the optic axes in the cases of those two caesium salts, and at the ordinary temperature; the uniaxial cross is exhibited in blue light (wave-lengths 450 for CsMg sulphate and 466 for CsMg selenate) at the ordinary temperature, and at 78° C. for sodium light. The interference figures afforded by caesium magnesium selenate are shown in the next figure.

The Molecular Refraction Constants probably show the optical relationships best of all, so the Gladstone constants are given in the next table.

It will be very clear from this simple table, and especially from the mean values in the last column, that the rubidium salt stands intermediate between the potassium and caesium salts as regards molecular refraction, and somewhat nearer to the potassium salt, as the refracting power increases more rapidly than in simple proportion to the change in atomic number or weight of the alkali metal.

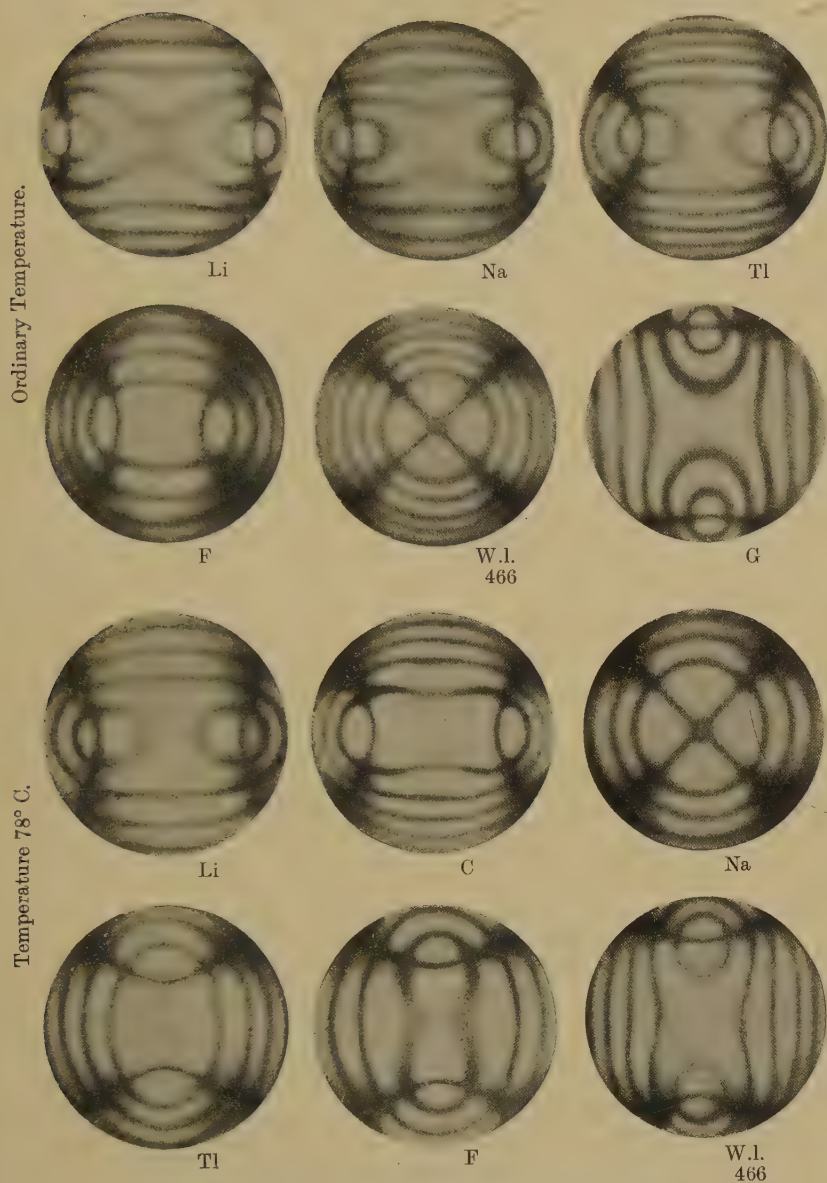


FIG. 49.—Interference Figures of CsMg Selenate.

Table of Molecular Refractions.

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C $\frac{1}{3}(\alpha + \beta + \gamma)$.
	α .	β .	γ .	
KNi sulphate .	93.37	94.92	97.50	95.26
RbNi .	99.11	100.43	102.26	100.60
AmNi .	100.34	101.55	103.00	101.63
CsNi .	109.35	110.19	110.91	110.15
TlNi .	120.98	124.21	125.02	123.40

Also, the values for the ammonium salt are very close to those for the rubidium salt, corresponding to the fact of their isostructural similarity.

The Optic Axial Angles are best compared in those groups which are free from the complication of crossed-axial-plane dispersion. The following table gives the optic axial angles in the case of the cobalt sulphate group, for instance.

Table of Optic Axial Angles.

	KCo sulphate.	RbCo sulphate.	CsCo sulphate.	AmCo sulphate.	TlCo sulphate.
Li . . .	68° 38'	75° 15'	81° 42'	82° 1'	66° 3'
C . . .	68 39	75 14	81 40	82 2	66 7
Na . . .	68 41	75 11	81 34	82 9	66 39
Tl . . .	68 44	75 8	81 29	82 17	67 8
F . . .	68 48	75 3	81 22	82 27	68 0

It is clear that this angle, for all the various wavelengths of light, for rubidium cobalt sulphate is intermediate between the angles between the optic axes of potassium cobalt and caesium cobalt sulphates. The ammonium and thallium salts afford optic axial angles somewhere near those of one of the other salts of the group, but no atomic number relationship is observed.

The Double Selenates afford precisely analogous results, the progression according to the atomic number and

atomic weight of the alkali metal being equally clear and definite. The absolute values of all the angles and constants are, however, moved on somewhat, and with regard to some of them considerably so, on the replacement of sulphur by selenium, but the relations of the three alkali-metallic salts of any one and the same group come out precisely the same as for the double sulphates, and the isostructure of the ammonium and rubidium salts is quite as clearly marked.

CHAPTER VI

GENERAL CONCLUSIONS REGARDING ISOMORPHISM

THE actual results of the research have been published in 28 papers, and 8 other memoirs were also published describing the new instruments devised for and employed in the research. A complete list of them is given as an appendix (p. 240).

It will now be desirable to summarise the outstanding results of the research on the two series of isomorphous salts which have been dealt with in the last two chapters, and to show how intimately they are connected with contemporaneous researches on the structure of the chemical atom.

The following main facts have been brought to light :—

(1) The crystals of the normal sulphates and selenates of the alkali metals potassium, rubidium, and cæsium, $R_2S[Se]O_4$, and the double sulphates and selenates of the hexahydrated series, $R_2M(S[Se]O_4)_2 \cdot 6H_2O$, in which R represents the same three alkali metals, form two very clearly marked and very well crystallised isomorphous series, the former of rhombic symmetry and the other of monoclinic. These series also include the analogous salts containing ammonium or thallium as the R-base, the NH_4 -base and the metal thallium in its thalious capacity replacing the alkali metal without more change of form than is observed when potassium and cæsium are interchanged.

(2) The characteristic feature of each of these two isomorphous series is that all the members exhibit the same system and class of symmetry, and the same facial "forms." The faces, however, are not inclined at iden-

tical angles, but at angles which differ by a clearly defined amount, which has never been found to exceed two and a half degrees between the extreme or any two members.

(3) In the case of the potassium, rubidium, and caesium salts of any one group these interfacial angular differences exhibit a regular progression, which follows that of the atomic numbers and atomic weights of the three interchangeable alkali metals. Moreover, the crystallographic elements, the volumes and edge-dimensions of the unit cells of the structural space-lattice (which is of the same type for all the members of each series), the position of the optical ellipsoid in the case of the monoclinic series (in which alone it is variable), the dimensions of the ellipsoid in both series, the refractive indices, the amount of double refraction, the molecular refractions, the optic axial angles in all cases uncomplicated by crossed-axial-plane dispersion, and the cubical coefficients of thermal expansion in the case of the rhombic series (for which alone they were determinable), in short, all the crystallographic properties which have been investigated, follow the same order of progression in the cases of the salts of the three alkali metals of each of the 18 groups dealt with.

In order to distinguish this very clearly-defined and regularly progressive kind of isomorphism the term "eutropic," from *εὐτροπή*, "a regularly progressive change," was suggested by Prof. Linck, in a review of the author's work, and it is so convenient a term that it has been adopted.

(4) The ammonium and thallium salts of any group do not belong to the inner "eutropic" set of the series, but are truly members of the isomorphous series in the sense of conclusion (2) and as defined in (5).

(5) AN ISOMORPHOUS SERIES may, in the light of this research, be defined as one the members of which have some definite chemical analogy and crystallise in the same system and class of symmetry, and develop the same

forms, the faces of which are inclined at angles which only differ by an amount not exceeding two and a half degrees, the amount being less the greater the symmetry. The most perfect type of isomorphism is that termed "eutropic," and occurs when the interchangeable chemical elements giving rise to the series belong exclusively to the same family group and type of series (odd or even) of the periodic classification. In such "eutropically" isomorphous series the whole of the crystallographic and physical properties exhibit a regular progression corresponding to that of the atomic numbers or atomic weights of the interchangeable elements.

(6) The ammonium salt of any group of either series has been found to be practically isostructural with the analogous rubidium salt, the volumes and edge-dimensions of the grosser structural units, the space-lattice cells, being almost identical. It is a remarkable thing that each of the two atoms of the intermediate alkali metal rubidium can thus be replaced by the NH_4 ammonium radicle group, without any very appreciable alteration of the crystal structure.

Another fact which has been observed continuously during the research is that:—

(7) Specific chemical substitutions invoke localised changes in the crystal structure, one crystal-axial direction frequently suffering much more change than the others, indicating that the chemical atoms occupy definitely localised positions in the crystal unit, the space-lattice cell, and therefore in the crystal molecule (the chemical molecule as it exists in the solid crystal state) or molecules (four in the rhombic series of sulphates and selenates, confirmed by X-ray analysis, and probably two at most, and possibly only one, in the double salt series) which compose the "cell." The actual positions of the atoms thus definitely fixed have, long after this fact was first published by the author, since been revealed by means of X-rays, which, by reason of their wave-lengths being

of the same order of dimensions as the atoms, are capable of reflection from or diffraction by the space-lattice-planes of atoms, at definite glancing angles for X-rays of specific ("monochromatic") wave-length, which enable the spacing of the planes to be calculated in absolute measure, and thence the unit cell dimensions and volumes.

(8) The cell dimensions thus obtained in absolute measure, in the case of the rhombic eutropic series of sulphates and of ammonium sulphate, which have been (alone as yet, of all the salts studied by the author) investigated by X-rays, agree exactly with the relative dimensions published long ago by the author.

(9) That the members of isomorphous series show real differences in their crystal angles is also quite independently proved by the fact that the replacement of sulphur by selenium, belonging to the same family of elements and odd series (3 and 5), is also accompanied by changes in the crystal angles and structural constants of a similar amount to that observed on replacement of the alkali metals by one another. Changes in the physical properties are also brought about. But all these changes leave the relations of the potassium, rubidium, and cæsium salts the same as for the sulphates.

Interchanges among the M-metals of the double salt series, magnesium, zinc, iron, manganese, nickel, cobalt, copper, and cadmium, also give rise to changes in the angles and structural and physical constants, but they are generally small, often surprisingly so, compared with the changes invoked by the interchange of the alkali metals.

(10) The above rules regulating the inter-relationships of members of isomorphous series allocate definite specific angles, crystal elements, structural cell-dimensions, and physical properties to each member. They consequently finally confirm and definitely establish as true the generalisation of Haüy, even for these very similar crystallisations, that "Every distinct crystallisable chemical substance

not of cubic symmetry (for that symmetry itself imposes identity of form) is endowed with a specific crystalline form peculiar and proper to itself." The rules also define the exact and limited sense in which Mitscherlich's principle of isomorphism is correct, and the extent, therefore, to which the literal meaning of the word "isomorphism" must be qualified. Both Häüy and Mitscherlich were largely correct, and the prolonged controversy is ended, with a large amount of credit to each. If full attention had long ago been given to the accurate goniometrical measurements of Wollaston, it need never have arisen.

Explanation of the Results.—The difference between the atomic numbers of potassium and rubidium, and also again that between the atomic sequence numbers of rubidium and caesium, has been shown to be 18 in each case. Now this difference of 18, meaning, as we know from the magnificent work of Moseley, 18 more electrons to the atom, and 18 more units of positive charge on its nucleus, corresponds precisely to a whole shell of electrons, or to two shells, according as the Lewis-Langmuir or the Bohr-Sommerfeld version of the atomic structure theory is correct. That is, when potassium is replaced by rubidium, and again when rubidium is replaced by caesium, one shell or two shells of electrons are being added on to the exterior of the atom of the alkali metal, obviously adding thereby to the diameter and complexity of the atom.

Also, W. L. Bragg has shown, as already mentioned in Chapter I, that the diameter of a chemical atom is a periodic function of the atomic number, and has published a table and curve, shown in Fig. 19 on page 33, corresponding thereto, of "Atomic Diameters," derived from the accumulated results of X-ray analyses. Although it is likely that the absolute values given in the list and curve may require revision as further observations are made, there is no doubt whatever that in the cases of structurally similar

compounds, such as the salts of either of the series investigated by the author, the relative values given for family group elements, such as those of potassium, rubidium, and caesium, are correct. Now the alkali metals occupy the successive maxima of Bragg's curve, and each maximum in turn is higher, representing a greater diameter of the atom, than its predecessor, so that, indeed, the atoms of caesium show the largest diameter of all the elements contained in the compounds up to now investigated by X-rays; and there is a regular progression in atomic diameter from potassium, through rubidium, to caesium. Now all this agrees perfectly with the supposition that one or two shells of electrons are added, 18 electrons in all, to the alkali metallic atom to make the atom of the next higher member of the family. Whatever version of the atomic structure theory be correct, and a blending of the two current versions seems to be the probable course of events, and a closer approximation to the truth, it is in any case a proved fact, due to the fundamental discovery of Moseley, that the atomic number represents not only the positive charge on the nucleus, but also the number of negative electrons surrounding the nucleus of the atom, and that whatever be their mode of arrangement or their modes of motion, this must inevitably mean addition to the size and complexity of the atom.

We may thus take it as undoubtedly true that when we replace potassium, of atomic number 19, by rubidium of atomic number 37, or the latter by caesium of atomic number 55, we are adding to the size of the atom, even although there be, as is probable, some consolidation. It stands to reason, therefore, that a crystal structure in which these atoms are, as we have seen, the dominant strongly electro-positive ones, must undergo some expansion when each of these changes is effected. And this progressive alteration in the size of the space-lattice cells, which has been directly, both crystallographically and by

X-rays, proved to be a fact, must in turn affect every property of the crystals, which will therefore likewise exhibit progressive change.

The alkali metals potassium, rubidium, and caesium each possess one more electron than is required to complete the outer shell of electrons respectively of argon (atomic number 18), of krypton (atomic number 36), and of xenon (atomic number 54). This extra outside electron has been shown to be the extremely chemically active combining agency of the alkali metal, when combination occurs with an electronegative element or group, such as chlorine Cl or the SO_4 radicle, probably actually passing over to the latter to complete a stable shell there, on the Cl or S atom for instance. The first new chemical compound produced, the chloride or sulphate of the alkali metal, is formed owing to the alkali metal being left with an excess of one unit of nuclear positive charge, while the other atom or radicle group then possesses a corresponding excess of negative charge, by reason of the acquirement of the electron to complete its outer shell, so that electrostatic action occurs between them. Something of this kind appears now to be agreed upon, in all versions of the atomic structure theory.

Thus it becomes clear that the choice of the alkali metallic salts for such a research as the author's was the best possible, and the results are fully explained by the contemporaneously acquired facts concerning atomic structure. At the time the work was commenced in the year 1890 there was no thought of such a wonderfully constructed miniature solar system as the chemical atom is now known to be, although atomic evolution was constantly present to the minds of such thinkers as the late Sir William Crookes. And perhaps even the author may be permitted to mention that so long ago as 1884 and 1886 he read two papers at the Royal College of Science (then the Normal School of Science and Royal School of

Mines) Debating Society on "the Evolution of Matter" and "The New Atomic Theory," which were subsequently (1887) published and brought up to date in the Science Schools Journal. Still this was all speculation, whereas we now have actual and more or less accurate knowledge. The remarkably dominant effect of the alkali metals is now readily comprehensible, and the reason for the relatively small effect of the interchange of the M-metals in the double salts also becomes clearly revealed; for these metals occupy the minima of the curve of atomic diameters and lie almost on the same horizontal line in the curve.

After the appearance of an account of the completion of the author's research on the two large isomorphous series, in the "Groth Festschrift" special volume of the *Zeitschrift für Kristallographie*, Prof. von Groth having taken the greatest possible interest in this research from its very commencement, Prof. Niggli, who had succeeded Prof. v. Groth as editor, gave a very suggestive review of the investigation, and pointed out that it can now be taken as proved that the homogeneity of crystal structure is not due to the arrangement of mere mass particles, but to the symmetry and structure of those particles themselves, the elementary atoms, and to the fields of force, orientated in character, which in consequence may be regarded as emanating from the atoms. From this it is clear, he says, that from crystal structure that of the atoms building up the crystal ought to be elucidated. He further particularly emphasises the importance of such accurate density determinations as were carried out in the course of this work, as an indication of the ranges or spheres of influence of the atoms of the elements which replace each other, and their progressive growth with the increase of atomic number. He then collates a large amount of further material from the data in Vols. I and II of Groth's "Chemische Kristallographie," making allowance for its less accurate character, and finally arrives at the relative spheres of

action and atomic diameters of a large number of elements, which agree remarkably well with those of W. L. Bragg.

Thus Crystallography now enters on a new sphere, no longer merely agreeing with the results of contemporaneous research on atomic structure, but itself entering into the research and supplying actual data for its further elucidation.

The other outstanding result of the research, the isostructure of the rubidium and ammonium salts, led the author to decide against adopting the celebrated Valency Volume Theory of Sir William Pope and Mr. W. Barlow, in the form in which its authors expressed it, that the sizes of the atoms entering into crystal structures were proportional to their chemical valencies. For if this were correct we should have for rubidium sulphate a valency volume of $2 + 2 + 8 = 12$, taking 1 for each monad rubidium atom, 2 for sulphur, and 2 for each oxygen atom; and for ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ we should have, taking nitrogen as triadic, a valency volume of $6 + 8 + 2 + 8 = 24$, twice as large as that for Rb_2SO_4 . But as they have been overwhelmingly proved to be isostructural the volumes are the same, and not one the double of the other. Happily, however, it is now proved by the author's results that atomic size really is a largely dominating factor, and by W. L. Bragg's, and Niggli's, determinations of atomic diameters that it is these diameters that are the correct ones for atoms entering into crystal structures. As these new atomic sizes correspond with the results of the author for the two great isomorphous series, at any rate as regards the relative sizes of the alkali metallic atoms, it would appear that the valency volumes should now be replaced by these atomic dimensions, valency thus not being an essential factor. Indeed, caesium, a monad, has the largest atoms of all those included in X-ray measurements. This theory of Pope and Barlow caused very great interest to be taken in crystallographic

research, and especially directed attention to it on the part of chemists, who had so unaccountably neglected it. It thus proved of great use, pending the time when, as has now happened, fuller light would be thrown on the subject.

The Missing Potassium Magnesium Chromate.—A curious circumstance has occurred with respect to one of the double chromates of the magnesium group, the rubidium, ammonium, and caesium salts of which were investigated by the author and Miss Mary Porter in the years 1911 and 1912. It was found impossible to obtain the analogous potassium salt, $K_2Mg(CrO_4)_2 \cdot 6H_2O$, reminding one of the difficulty, eventually so happily overcome as already described, of obtaining potassium iron selenate. The results showed that the relations between the three salts obtained were precisely analogous to those for rubidium, caesium, and ammonium salts of any group of the double sulphates and selenates. Still it was a pity not to be able to include the potassium salt.

In 1919 A. Duffour described in the *Comptes rendus* of the French Académie des Sciences * how that he had succeeded in preparing the missing salt, in a very cold place, and that when collected immediately the crystals were clear and limpidly transparent, of yellow colour and of considerable size; but that if left in the mother-liquor they became invaded and swallowed up by small spherulitic opaque crystals of a triclinic dihydrate. Also, when removed from the mother-liquor they became opaque in less than half a day, and more quickly if the temperature exceeded $10^\circ C$. He was able to get a few measurements, and these fall into line, as expected, with the results for the rubidium, caesium, and ammonium salts, being related to them precisely as the potassium salts of all the sulphate and selenate groups have been to their rubidium, caesium, and ammonium analogues. The author has made many attempts to repeat Duffour's experiments, but so far has

* *Comptes rendus*, 1919, 169, 73.

not obtained the hexahydrated crystals. It may be that some day the missing potassium-manganese and potassium-cadmium sulphates and selenates may be obtained, when it will be interesting to see how the author's predicted constants for those salts agree with any possible measurements that should be made. It appears only too likely, however, that the limiting upper temperature for the existence of those salts is just below the freezing point of water, whereas for potassium-iron selenate and potassium-magnesium chromate it is just above freezing point.

The Alkali Permanganates and Perchlorates.—Two other groups of orthorhombic salts of the alkalies, the permanganates and perchlorates of potassium, rubidium, caesium, and ammonium, and also thallium perchlorate, have been investigated by Muthmann and by Barker respectively, but as far only as their exterior angles and their volume constants are concerned. As regards these, however, the results were similar to the author's for the sulphates and selenates, and they are given in the next table.

Table of Permanganates and Perchlorates.

	<i>m : m.</i>		<i>c : q.</i>		<i>c : r.</i>		Mol. vol.	χ .	ψ .	ω .	ξ .
{ KClO ₄ . RbClO ₄ . CsClO ₄ . AmClO ₄ . TlClO ₄ .	76° 1'	52° 1'	39° 19'	54.91	3.7360	4.7878	6.1307	3.0365			
	77 5	—	38 57	61.33	3.9244	4.9264	6.3447	3.1492			
	78 31	52 23	38 27	70.05	4.1625	5.0929	6.6086	3.2888			
	76 50	52 1	38 55	60.19	3.8959	4.9117	6.2909	3.1346			
	77 10	—	38 57	62.66	3.9964	5.0093	6.2606	3.2040			
{ KMnO ₄ . RbMnO ₄ . CsMnO ₄ . AmMnO ₄ .	77 8	52 24	39 9	58.53	3.8555	4.8360	6.2779	3.0924			
	79 28	53 7	38 48	63.23	4.0362	4.8565	6.4704	3.1574			
	81 56	53 53	38 17	70.04	4.2551	4.9005	6.7161	3.2450			
	78 28	52 47	38 53	62.13	3.9757	4.8698	6.4126	3.1433			
{ Barytes Celestite Anglesite	78 23	—	—	52.0	3.6509	4.7899	5.9472	3.0113			
	75 58	—	—	46.8	3.5349	4.5931	5.7649	2.8980			
	76 17	—	—	48.2	3.5743	4.5520	5.8694	2.8938			

It will be seen that the rubidium salt values are always intermediate between those of the corresponding potassium

and cæsium salts, and that the ammonium and thallium salts have values very close to those for the rubidium salt of the same group.

It is obvious, therefore, that—given a eutropically isomorphous series, of which the interchangeable elements belong to the same family group and same odd or even series of that group of the periodic table of the elements, and the members of which are all built up on identical symmetry lines, their space-lattice being of the same type and its unit cells occupied by one molecule or the same small number of chemical molecules—the law of progression with the atomic sequence numbers of the interchangeable elements should prove to be a general law of nature. The salts must, however, as stipulated, be strictly comparable as regards structure, or the law cannot operate. And it is for this reason that the law has not been discovered before, the crystals of so many of the well-known series not being composed entirely of strictly comparable structures, although their system of symmetry may be the same.

The Alkali Haloid Salts.—An excellent case in point is that of the haloid compounds of the alkali metals, all belonging to the cubic system. Now sodium chloride NaCl, potassium chloride KCl, and rubidium chloride RbCl, are apparently strictly comparable, their crystals having the well-known face-centred cube structure, with four molecules to the unit cell as determined by Sir William Bragg. But cæsium chloride, CsCl, has the centred-cube structure with one molecule only to the cell, and so is not comparable to the others just mentioned. Ammonium chloride, NH_4Cl , has been shown by I. Langmuir and G. Bartlett * to have two forms, a low temperature one resembling cæsium chloride, and a high temperature one (250°C) resembling sodium chloride. They have shown that the NH_4 group replaces the alkali metallic atom as a whole radicle, which behaves as a unit or entity, just as do

* *Journ. Amer. Chem. Soc.*, 1921, 43, 84.

the organic radicles. Similarly, sodium bromide NaBr , and sodium iodide NaI , possess the sodium chloride structure, as do likewise the bromides and iodides of potassium and rubidium, KBr , KI , RbBr , and RbI ; but caesium bromide, CsBr , and caesium iodide, CsI , resemble caesium chloride. Thallium chloride has also been X-rayed, and proved to possess the caesium chloride structure. The whole haloid series, therefore, is not a continuous one with analogous structures throughout, and the morphological and physical constants are in consequence not all continuously progressive.

Now this has been more than once quoted as a case disproving the general law of progression which the author has established. It will be clear from these facts, therefore, that great care has to be instituted in order to avoid drawing mistaken conclusions about the compounds of family group elements. It often happens, as in the haloid salts, that the temperature limit of existence or stability is reached in the middle of a series, and that the following member or members have the new structure which is alone possible at the ordinary temperature, and are therefore not strictly comparable with the other members as regards their morphological and physical constants. There do not appear to be many series so free from complication as the rhombic sulphates and selenates of the alkali metals, and the monoclinic hexahydrated double sulphates and selenates.

A study of the chlorates, bromates, and iodates of sodium and potassium, by G. H. Smith shows that similar relations exist between these salts as with the haloids, some exhibiting the sodium chloride type of structure and others that of caesium chloride. Sodium chlorate NaClO_3 and bromate NaBrO_3 belong to the sodium chloride set, with four molecules to the unit cell, while sodium iodate NaIO_3 belongs to the caesium chloride set with one molecule to the cell. Potassium chlorate, KClO_3 , is monoclinic, but

the sodium chloride type persists with monoclinic deformation. Potassium bromate, KBrO_3 , is ditrigonal-pyramidal but of pseudo-cubic type, having the structure, deformed, of caesium chloride, with one molecule to the cell. Potassium iodate, KIO_3 , is similar, but monoclinic pseudo-cubic, and also belongs to the caesium chloride set. In all these cases the radicle ClO_3 , BrO_3 , or IO_3 , acts as a unit simply replacing the chlorine, bromine, or iodine atom. Each radicle is surrounded, but not now equidistantly, by six or eight oppositely charged radicles, according as the NaCl or CsCl type obtains.

Jaeger's Series.—A particularly interesting new series of isomorphous salts has been prepared and studied by F. M. Jaeger of Groningen, which illustrates the smallness of interfacial angular differences in the systems of higher symmetry, assisted by special circumstances relating to atomic structure. The crystals belong to the pyramidal class 25 (the apatite class) of the hexagonal system, and the interchangeable elements are the rare-earth metals yttrium, cerium, lanthanum, neodymium, praseodymium, samarium, europium, dysprosium, gadolinium, erbium, neoytterbium, and thulium; they are the ethyl sulphates of these metals, which may be represented by R in the general formula of the salts $\text{R}_2'''(\text{SO}_4 \cdot \text{C}_2\text{H}_5)_6 \cdot 18\text{H}_2\text{O}$. The angular differences were so small that Jaeger considered they fell within the limits of experimental error, and their common axial ratios he gives as $c : a = 0.5062 \pm 0.0012$. Besides the high symmetry, however, which alone would not suffice to account for the differences being so very small, and also the large mass of the remainder of the complex molecule, there is a special reason for the remarkably small interfacial angular differences between these salts. Absolutely contrariwise to the case with the alkali metals, the atoms of which have already been shown to be enlarged at every step in passing from potassium through rubidium to caesium by the addition of either

one (according to Langmuir) or two (according to Bohr) whole shells of electrons, 18 electrons at each step, the rare-earth elements, which occupy two whole periods of the periodic table, are not formed by the addition of electrons to the outer shell, but by the internal addition of electrons, without increasing the size of the atoms. As chemical properties are essentially functions of the outer electrons, the atoms of the rare earths possess such similar properties that the most extraordinary refinements of fractionation processes, and great expenditure of time and labour, are needful in order to separate them and to isolate the individual elements. This case is, therefore, the antithesis of that of the author's two series of alkali-metallic isomorphous salts.

CHAPTER VII

PARALLEL GROWTHS, OVERGROWTHS, AND MIXED CRYSTALS

THE conditions for *Parallel Growths and Overgrowths* of one substance on another, and of intergrowths, "mixed crystals" as they are called, have formed the subject of many and prolonged researches, and it is only as the result of recent work that they have been established satisfactorily. Perhaps the best instance of the phenomenon of parallel growths is that of sodium nitrate on calcite; for the host in this case is a mineral which is insoluble in and unattacked by the saturated solution of the salt which is allowed to crystallise on it. A photograph of such crystals of sodium nitrate deposited on a face of the rhombohedron of calcite is shown in Fig. 50.

Sodium nitrate NaNO_3 and calcite CaCO_3 both crystallise in the ditrigonal scalenohedral class 21 of the trigonal system, and their rhombohedral angles α and rr , axial ratios $a : c$, molecular volumes V , which represent the relative volumes of the rhombohedral lattice cells, and their topic axial ratios χ , representing the cell-edge dimensions, are given below :—

	Angle rr over rhombohedral polar edges.	Rhombo- hedral axial angle α .	Axial ratio $a : c$.	Volume V .	Topic axial ratio χ .
NaNO_3 .	$73^\circ 37'$	$102^\circ 42'$	1:0.8297	37.8	3.461
CaCO_3 .	$74 \quad 55$	$101 \quad 54$	1:0.8545	36.77	3.394

It will be obvious how very close together are the crystal elements, and the volume and dimensions of the structural-

unit cell. They are much closer than those of any other members of the calcite group of minerals are to those of sodium nitrate, so that no parallel growths of the latter are formed on any besides calcite. Thus the volumes for chalybite FeCO_3 , calamine ZnCO_3 , and rhodochrosite MnCO_3 , are respectively 29.53, 28.81, and 31.05, and their topic axial ratios are 3.193, 3.174, and 3.242 respectively.

T. V. Barker has made experiments with a large number of salts, and has definitely proved that the formation of

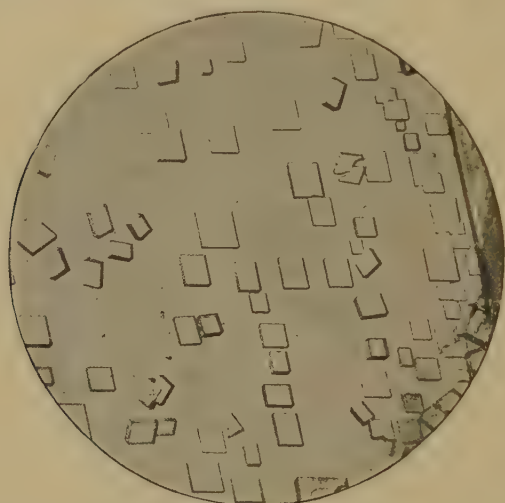


FIG. 50.—Sodium Nitrate Crystallised on Calcite.

parallel growths is dependent on close similarity, congruency, in shape and size of the unit cells of the structural space-lattice of the crystals. Not only must the system and class of symmetry be the same, but also the volumes and edge-dimensions of the unit cells. That is, the molecular volumes, absolute volumes, topic axial ratios (relative dimensions), and absolute edge-dimensions must closely agree.

Overgrowths occur when this closeness is very near to identity, the nearer to identity the more perfect the overgrowth, and the possibility of complete intimate admixture

if both substances are soluble in water, or the same solvent whatever it may be.

Excellent overgrowths of magnesium sulphate are obtained on zinc sulphate crystals, when the latter are immersed in a slightly supersaturated solution of the former. The molecular volumes are very close indeed, namely 146.7 for $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 147.1 for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Also there is the very well known case of potassium chrome alum crystals, of which the molecular volume is 542.2, continuing to grow in a solution of potassium aluminium alum, which possesses the molecular volume 541.6. In this case the former salt has a fine purple colour, while the latter salt is colourless, so that the former can be seen clearly inside the latter, and a cross-section shows the two very obviously differentiated.

There is also the important case of the triclinic plagioclase feldspars, albite the soda feldspar $\text{NaAlSi}_3\text{O}_8$, and anorthite the lime feldspar $\text{CaAl}_2\text{Si}_2\text{O}_8$, the former having the molecular volume 100.1 and the latter the molecular volume 101.5. Zonal growths of one of these on the other are very common, often taking the form, as seen in rock sections, of regular bands surrounding a nucleus; and these two feldspars are the end members of a whole series of plagioclase feldspars containing both soda and lime, but they are not truly different minerals, although they have been given distinctive names, such as oligoclase, andesine, and labradorite, but isomorphous mixtures in different proportions of the two well-defined mineral species albite and anorthite, with optical properties of a distinctive character. "Solid Solution" is a term, first applied by van 't Hoff, which has been given to such close mixtures of isomorphous compounds, although the term appears to the author to be no more satisfactory than the so-called "liquid crystal" term is for the curious liquids with which Lehmann has made us so familiar. But if by "solid solution" the idea is merely conveyed that the physical

properties alter continuously with the chemical constitution, then it accords with the facts, as derived from the results of the latest investigations, including the use of X-rays.

This brings us to a more irregular kind of isomorphous admixture, known as "vicarious." It frequently happens that a mineral is found in nature beautifully crystallised, and which is essentially a definite specimen of that mineral. But on making a careful chemical quantitative analysis, it is found that besides the expected base or bases, or acid radicle, there are also small quantities of other elements, bases or acids present, the elements being those of the same family group, which form oxides of basic or acidic character which readily replace each other. If a chemical formula were calculated directly from the analysis as it stands, the formula would be grotesque, having a large number of atoms of one base to only one or two of the other or others; whereas, if these small quantities were each calculated into their equivalent of the main base or bases a simple and reasonable formula would be arrived at. A good example is the series of garnet minerals, $R''_3R'''_2(SiO_4)_3$, which crystallise with cubic symmetry in rhombic dodecahedra and icositetrahedra. There are five principal members, in which R'' is calcium, magnesium, or ferrous iron, and R''' is aluminium, ferric iron, or chromium, their names and compositions being the following :—

Grossular . . .	$3CaO \cdot Al_2O_3 \cdot 3SiO_2$
Pyrope . . .	$3MgO \cdot Al_2O_3 \cdot 3SiO_2$
Almandine . . .	$3FeO \cdot Al_2O_3 \cdot 3SiO_2$
Andradite . . .	$3CaO \cdot Fe_2O_3 \cdot 3SiO_2$
Uvarovite . . .	$3CaO \cdot Cr_2O_3 \cdot 3SiO_2$

Many garnets, however, prove on analysis not to be strictly any one of these minerals, but are essentially one of them in which either the particular R'' or the R''' is more or less replaced by one of the other two metals of the same type.

From the foregoing it will be clear that the formation of parallel growths, overgrowths, and mixed crystals is dependent on more or less close similarity of the crystal structure, the unit cells of the space-lattice requiring to be not only strictly of the same type but closely isostructural, as regards the volume and edge-dimensions of the parallel-epipedal cells. The first approach to identity induces parallel growths, still closer approximation brings about overgrowths and zonal growths, and the closest approach causes great facility in the formation of mixed crystals.

The Nature of Mixed Crystals.—Some very interesting further facts, however, have been derived from the prolonged researches on mixed crystals. If we take, for instance, the case of the rhombic series of alkali sulphates and selenates, the volume constants and cell-edge dimensions of which are given on pages 94 and 95, it is found that the two end members of either group, the potassium and cæsium salts, which in the progression according to atomic number of the alkali metal are the furthest apart in regard to the relative and absolute dimensions of the space-lattice cells, never form mixed crystals at all, nor even any parallel growths or overgrowths. But the intermediate rubidium salt will form mixed crystals with either the potassium or the cæsium salt, but with some difficulty, however, and parallel growths readily, the differences in cell dimensions being less in these cases. On the other hand, the ammonium and rubidium salts, which have been shown to be remarkably isostructural, will form mixed crystals with the greatest ease, and in all proportions. These facts are not only due to the author's observations; they were quite independently observed and published by T. V. Barker and by G. Wulff of Moscow. There is thus the fullest confirmation of their truth. That the absolute dimensions of the cells, as well as the relative sizes, in the cases of the rubidium and ammonium salts of the same group, are nearly identical was proved by the X-ray analysis of the

crystals supplied by the author to Sir William Bragg, in whose laboratory the analysis was carried out as already described.

The author's experience with the selenates of rubidium and ammonium was really remarkable. For ammonium selenate, as already described in Chapter IV, does not usually crystallise like the other nine salts of the series, in rhombic crystals, but in monoclinic, being dimorphous. Yet when mixed in solution in water with rubidium selenate the crystals deposited are rhombic, even when they contain as much as sixty per cent. of ammonium selenate, such crystals being large, well formed, lustrous, and quite transparent. It has been mentioned that the first crystals of ammonium selenate to be measured, by Prof. von Lang, were the rhombic variety, due to their admixture with ammonium sulphate, which also forms mixed crystals with ammonium selenate, as was discovered by the author on re-examination of Prof. von Lang's specimens forty years afterwards. The monoclinic variety was also present, as needle-shaped prisms, intermingled with the larger and better-formed rhombic crystals. As Prof. von Lang had not noticed them at the time, it is quite possible that they had formed in the long interregnum, by decomposition of some of the crystals of the less stable rhombic form.

The question that has agitated most of the workers on the subject of mixed crystals has been whether the two substances which mix in the crystalline condition do so in alternating layers of the two substances—a view advocated by Retgers—or as a much more intimate intermingling, to form a crystal with intermediate angles and physical properties, as of one single substance. This latter view has been held by Wulff, Barker, Gossner, from work on the silico-fluorides and stannofluorides of zinc and nickel, and the author. They consider that—the essential condition being extreme closeness of congruency of the structure cells, and the two substances being free, in forming mixed crystals

(as sodium nitrate and calcite are not, the calcite molecules being already fixed in the relatively hard mineral when the sodium nitrate parallel growths are deposited on them), to approach and accommodate themselves to each other—the two substances actually take advantage of this freedom to do so, the force of crystallisation bringing about actual equalisation of the molecular volumes and the cell-edge dimensions. The amount of change undergone in such a process is only of the same order as that of the thermal expansion, which the author had directly determined for the rhombic sulphates of the alkalies.

The matter has eventually been settled by X-ray analysis. Two independent X-ray investigations were carried out by Vegard and Schjelderup with mixtures of the cubic alkali halides, potassium chloride KCl, potassium bromide KBr, and ammonium bromide NH_4Br , and by Rinne with the rhombohedral carbonates, the cubic haloid salts of lithium, sodium, potassium, rubidium, and cæsium, and several mixtures of metals. In all cases the mixed crystals were found to reflect X-rays as single entities, the spectra being, not double as from two different structures, but single and as clearly defined as for a pure single substance. The atoms of the two substances are probably most intimately disseminated throughout the structure, in the proportions corresponding to the relative quantities of the two substances present.

Especially valuable confirmation of this happy solution by X-ray analysis, of the difficult question of mixed crystals, is afforded by the observations which have been accumulating in the meantime concerning the optical properties of mixed crystals. Taking first the simplest case of the singly refractive cubic crystals, both Fock and Dufet have studied the refractive indices of mixtures of potassium and thallium alums, and the result has been to show that the single refractive index varies directly proportionally to the relative amounts of the two salts

present, that is, directly with the composition. Soret also obtained a like result for mixtures of potassium and ammonium alums.

Passing now to optically uniaxial birefringent crystals, the mixtures of the tetrahydrated strontium and lead dithionates have been investigated as regards their two refractive indices by Fock, and with reference to their optical rotatory power by Bodländer, and as regards both properties direct proportionality to the composition was observed.

Of optically biaxial doubly refractive substances, isomorphous mixtures of the rhombic magnesium, zinc, and nickel sulphates, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, have been very fully examined by Dufet as regards their three refractive indices, and their linear dependence on the proportions of the salts present was clearly established.

A particularly interesting case has been investigated by Dufet, Lavenir, Des Cloizeaux and Wyruboff, that of the Seignette salts, sodium ammonium tartrate, $\text{NaNH}_4\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, and sodium potassium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, which crystallise in the orthorhombic system, the digonal bisphenoidal class 6, with the axial ratios $a : b : c = 0.9233 : 1 : 0.4200$ and $0.8317 : 1 : 0.4296$ respectively. The double refraction of these salts is so feeble, the extreme refractive indices α and γ being so close together, and the dispersion of the optic axes for different wave-lengths of light consequently so large, that very slight alteration of the indices causes relatively very large changes in the optic axial angle. Moreover, the optic axes are separated in the a (100) plane for the first salt, and in the b (010) plane for the other salt. The change of optic axial angle, therefore, would form a very sensitive indicator of any such change in the refractive indices, should any be brought about by admixture of the two salts in "solid solution."

The experiments resulted in showing that the refractive

indices did change on admixture of the two salts in mixed crystals, and the values were in direct linear proportions to those of the two salts in the mixtures. For a small proportion of the sodium ammonium salt in a larger quantity of the sodium potassium salt the optic axes are approached near to each other. For a certain larger proportion of the sodium ammonium salt the crystals show the uniaxial figure in red light. On further addition of that salt to the mixture the axes in red light are now separated in the (100) plane, while for orange the axes are crossed, and for the other colours of the spectrum they are still separated in the (010) plane. Indeed, as more and more sodium ammonium salt is added the cross becomes formed for yellow, green, blue, and violet in turn, after which, with still further relative quantities of sodium ammonium salt the optic axes are separated entirely in the plane (100), until eventually the pure sodium ammonium salt is attained, with its own specific values for the optic axial angle in the plane (100). This behaviour of the Seignette salts affords very beautiful screen pictures with the lantern polariscope in convergent polarised light, and the phenomena in monochromatic light is excellently followed with the aid of the author's monochromatic illuminator, with which it is possible to record the exact wave-lengths for every production of a uniaxial figure. Mixed crystals showing the uniaxial cross for convenient middle parts of the spectrum have been shown in many demonstrations, and are currently known as triple tartrate crystals, as the three bases sodium, potassium, and ammonium are all present. Two such section-plates of "triple tartrate" possessed by the author produce the uniaxial cross and circular rings for yellowish green light of the wave-lengths 0.000533 and 0.000528 mm. respectively, quite near to the wave-length of the green thallium line, 0.000535 mm. Fig. 49 on page 123 will assist in appreciating the phenomena.

H. E. Buckley has described some very interesting

optical anomalies which these Seignette salts show when freshly prepared, but which disappear in a short time, one to twelve weeks in different specimens, the optic axial interference figures showing crossed dispersion, that associated with a monoclinic crystal. The author's specimens, being some years old, do not show this irregularity. It would appear as if some time is taken by the molecules in finally adjusting their two separate structures to form the single intermediate one.

E. Mallard studied the optic axial angle phenomena of another pair of rhombic salts, the mixed crystals of which gave similar results, namely, potassium sulphate and ammonium sulphate. The optic axes of K_2SO_4 lie in the plane (100), and those of $(NH_4)_2SO_4$ in the plane (010), the first median line (acute bisectrix of the optic axial angle) being the axes a and c in the two respective cases. As ammonium sulphate is added in progressive quantities the optic axes, as seen in air through a section-plate perpendicular to the axis b , the second median line, approach one another in the plane (100), until, when 19 per cent. of ammonium sulphate is present, they unite in the centre to form the uniaxial cross; as more and more ammonium sulphate is present the axes spread out again, but in the plane (001). When still more is contained in the mixed crystal the axes separate so much that the normal to the plate (axis b) ceases to be the first median line and axis a becomes the acute bisectrix instead, as for the pure ammonium salt. The optic axes then close in to this crystal axis a , and coalesce, producing the uniaxial figure, after which they again separate, and in the plane (010), eventually attaining in that plane the characteristic separation of pure ammonium sulphate. The whole phenomena are quite continuous, and agree with proportional effects corresponding to the amount of admixture of one salt with another. Mallard likewise studied mixtures of potassium sulphate and potassium chromate, and also

with them observed continuous effects corresponding with direct proportionality.

The latest of these researches on mixed crystals is one by Miss M. W. Porter * on mixtures of two monoclinic salts, ammonium magnesium chromate and rubidium magnesium chromate, which were measured and described by the author and Miss Porter in the year 1911.† Their molecular volumes are so extremely close, 216.9 and 215.5, that they mix perfectly in all proportions to form excellent homogeneous crystals, while their optical properties are sufficiently different to afford clear and definite results for mixed crystals of specific composition, which is practically that of the solution from which they crystallise.

The results showed that the crystal angles, and the elements calculated from them, varied continuously with the composition; for instance, the important monoclinic angle β changed from $104^{\circ} 52'$ for the rubidium salt to $106^{\circ} 9'$ for the ammonium salt, as crystals containing growing amounts of the latter salt were measured. The optic axial angles behaved like those of potassium and ammonium sulphates. The optic axes lie in the symmetry plane b (010) for the ammonium salt, at an angle of separation of $45^{\circ} 8'$, the acute bisectrix being $3^{\circ} 27'$ in front of the vertical axis c . For the rubidium salt the optic axial plane is perpendicular to the symmetry plane, and the acute bisectrix is the symmetry axis b , the double refraction being negative, while for the ammonium salt it is positive. The obtuse bisectrix lies $48^{\circ} 10'$ behind the axis c . In a mixed crystal with 19 per cent. of the ammonium salt the sign of the double refraction has already become positive, and the symmetry axis is no longer the acute bisectrix. With growing amounts of the ammonium salt the optic axial angle steadily diminishes, until with 95 per cent. it becomes zero, the uniaxial figure being afforded and the α and β refractive indices becoming equal; the plane of the

* *Proc. Roy. Soc., A.*, 1925, **109**, 78.

† *Min. Mag.*, 1912, **16**, 169.

axes has also moved forwards till the γ direction passes in front of axis c . For mixed crystals with between 95 and 100 per cent. of the ammonium salt the optic axes open out in the symmetry plane, with gradually increasing angular separation. Thus the optic axial angle phenomena change quite regularly with the composition.

Likewise the refractive indices show a regular change, from (for sodium light) $\alpha = 1.6216$, $\beta = 1.6330$, $\gamma = 1.6349$ for the rubidium salt to $\alpha = 1.6363$, $\beta = 1.6371$, $\gamma = 1.6528$ for the ammonium salt. As regards that index which corresponds to the direction of the symmetry axis, which alone does not vary in orientation in a monoclinic crystal, the values lie on a straight line, showing direct proportionality to composition. For the other two indices, they lie on lines which are slightly curved, but vary regularly also with the composition, although not precisely linearly. These results thus confirm, and extend to monoclinic crystals, the work of Lavenir, Dufet, and Mallard on orthorhombic mixtures, in so far as they show that, in a monoclinic series of mixed crystals, there exists a linear relation between the refractive indices of mixtures and of their component salts for that direction for which alone they are comparable throughout the series. While the research fails to distinguish between volume and molecular percentage, it shows that the variation of the indices is proportional to one or other of these, rather than to percentage by weight.

Thus the phenomena of mixed crystals are now cleared up in a very satisfactory manner, and the conditions for admixture, close congruency-similarity of the volumes and edge-dimensions of the space-lattice unit cells, definitely established.

Before leaving this subject of parallel growths and mixed crystals, it should be mentioned that an interesting case of possible isomorphism has been pointed out by T. V. Barker, which if correct, is one of fortuitous iso-

structure rather than chemical similarity. It is that of barytes, BaSO_4 , and potassium perchlorate, KClO_4 . On page 136 a table is given of the morphological constants of the perchlorates of the alkalis, followed by similar constants for the barytes group. If the constants there given for potassium perchlorate are compared with those for this barytes orthorhombic group of minerals, barytes, celestite SrSO_4 , and anglesite PbSO_4 (anhydrite CaSO_4 is not a member of the group, as it has a different structure and cleavage), it will be observed that barytes differs but little from potassium perchlorate in molecular volume and topic axial ratios, the critical constants for isostructure, and these two salts exhibit indeed closer approximation than is observed between any other members of the perchlorate-permanganate group and the barytes group. Now potassium perchlorate forms beautiful parallel growths of well-defined miniature crystals on the face of a barytes crystal, and is the only salt referred to in the table on page 136 which does. Hence, just as in the case of sodium nitrate and calcite, we have here a case of isostructure without chemical analogy, and it is doubtless better to speak of isostructure than of true isomorphism.

Barker and others have suggested that a considerable number of such cases of isostructure may be regarded as of isomorphism, if the latter term be allowed to include compounds of which Werner has explained the constitution on the lines of his co-ordination theory. Werner's idea is represented by placing certain portions of the formulæ of these more complicated compounds within square brackets, and the bracketted portions are often found capable of replacing each other. Thus sodium nitrate and calcite would be written $\text{Na}[\text{NO}_3]$ and $\text{Ca}[\text{CO}_3]$, and the two metals, and also the two portions in brackets, would each be regarded as capable of interchange in the crystal structure. Similarly potassium perchlorate and barytes could be written as $\text{K}[\text{ClO}_4]$ and $\text{Ba}[\text{SO}_4]$. Barker has

shown that a third compound, potassium borofluoride, $K[BF_4]$, is also capable of forming parallel growths, and seems as if it should be regarded also as isostructural with barytes, and on writing its composition in the Wernerian manner an explanation appears to be afforded. Confirmation as regards sodium nitrate and calcite has certainly been afforded by Sir William Bragg's X-ray analysis, for the NO_3 and CO_3 radicle groups, and also the Na and Ca atoms, appear to replace each other at the rhombohedral space-lattice nodes. But in any event the isostructure as regards the shape and dimensions of the space-lattice cells is the dominant fact, and it is not very material whether it be called isomorphism or not, so long as it is clearly understood that isostructure is meant, and that chemical analogy is only that on Wernerian lines and not true chemical family-group-and-series close relationship.

Two more complicated cases of co-ordination ideas explaining similarities of crystal structure may perhaps be quoted. The complex substance hexammine-nickel chloride $[Ni(NH_3)_6]Cl_2$ has been shown by Wyckoff to have a similar structure to fluorspar, CaF_2 , which is like the diamond, but with the centres of all the cubelets filled with atoms instead of only alternate ones; the calcium atoms are arranged in the main face-centred cube lattice and the fluorine atoms occupy the eight cubelet centres into which the face-centred cube divides up. The idea is that the portion of the hexammine-nickel chloride formula enclosed in the square brackets replaces the calcium atoms, and the chlorine atoms those of fluorine. Potassium chloroplatinate written as $[PtCl_6]K_2$, and the more complicated compound hexahydrated zinc bromate $[Zn(H_2O)_6](BrO_3)_2$ also follows the fluorspar type of structure. The six ammonias surround the nickel atom in the regular octahedral manner in the first of the three compounds, and the six molecules of water of crystallisation appear to act similarly in the third compound.

The other case is that of the spinels, $\text{Al}_2[\text{MgO}_4]$, which were shown independently by Bragg and Nishikawa to possess a structure also derived from that of the diamond. Wyckoff has since also shown that silver molybdate $\text{Ag}_2[\text{MoO}_4]$ is built up on the same plan, and Dickenson has added also the case of the complex cyanide $\text{K}_2[\text{Zn}(\text{CN})_4]$ as constructed on this same spinel type. In all these cases the part of the formula enclosed in square brackets is supposed to play an analogous part in the crystal structure. Much attention is being given just now to these co-ordination formulæ, and they may lead to the comprehension of apparent isomorphism in many difficult cases. It will not do, however, to carry these analogies too far.

Incidentally now, practically all the important groups of isomorphous salts and minerals have been referred to, and each in order to demonstrate some particular feature of isomorphism, so that the main features of this highly interesting and important phenomenon will, it is hoped, now have been made clear.

In conclusion, reference may be made to the fact that isomorphism is directly responsible for the ease with which, under properly understood and regulated conditions, good crystals other than those of natural minerals can be grown for crystallographic investigation. For such crystals must be prepared from metastable solutions, and these are set crystallising by the falling into them of crystal germs from the air, either of the same substance or, probably more frequently, of an isomorphous or isostructural one. These crystal-particles have been shown to be of almost incredible minuteness, direct determinations having indicated a weight of only 10^{-9} to 10^{-12} gramme, and in the case of sodium sulphate a determination only gave a weight of 10^{-18} gramme. It is one of the marvels of nature that such minute yet perfect crystals should be present in our atmosphere.

CHAPTER VIII

ISOGONISM, POLYMORPHISM, AND POLYSYMMETRY

Isogonism or Morphotropy.—Certain chemically related substances, especially organic compounds, which are not so definitely connected as are the isomorphous series referred to in preceding chapters, have been shown to exhibit some similarities of crystalline form which are of more than passing interest. The similarities generally occur with respect to certain zones of faces only, and in the case of crystals of the three lower systems, rhombic, monoclinic, and triclinic, with respect to one of the axial ratios only, $a : b$ or $c : b$. It was at one time supposed that the similarities were real, although the two substances might belong to two different crystal systems. This view was based on the observations of Laurent and Nicklès during the years 1842 to 1849. Laurent in 1842 and 1845 found that certain organic substances, a good example being naphthalene tetrachloride $C_{10}H_8Cl_4$ and chlornaphthalene tetrachloride $C_{10}H_7Cl.Cl_4$ which are respectively monoclinic and rhombic, form crystals which, although they belong to different systems, exhibit but very slight angular differences as regards certain principal interfacial angles; for instance in the case just quoted the prism angle is only $45'$ different, that of the tetrachloride being $109^\circ 0'$ and that of the chlortetrachloride $109^\circ 45'$. Nicklès likewise showed that the barium salts of the fatty acids crystallise in different systems but with prism angles ranging only between 98° and 100° . But he failed to point out that these salts crystallise with different amounts of water of crystallisation, and it is an important fact in chemical

crystallography that the difference even of one molecule of water of crystallisation invariably alters the crystalline form entirely, so that his salts were not at all comparable. As a matter of fact when the water of crystallisation, if any, is the same, the members of homologous series differing by steps of CH_2 often show much closer resemblances than those indicated by Nicklès.

In the year 1848, however, Pasteur found several zonal similarities among some related tartrates, and thus confirmed the reality of isogonism. But discussion, of a very unsatisfactory nature, being without much new experimental basis, continued until as late as the year 1870, when Prof. P. von Groth, of Munich, the founder and editor for fifty years of the *Zeitschrift für Krystallographie*, made a systematic experimental investigation of the question, choosing the derivatives of benzene for his study.

He showed first of all that benzene itself, C_6H_6 , a liquid at ordinary temperatures, crystallises in very cold weather in rhombic crystals having the axial ratios $a : b : c = 0.891 : 1 : 0.977$. On replacing one or two of the atoms of hydrogen by hydroxyl groups OH , phenol $\text{C}_6\text{H}_5(\text{OH})$ and resorcinol $\text{C}_6\text{H}_4(\text{OH})_2$ are obtained, crystallising also in orthorhombic crystals. Phenol is not easily obtained in measurable crystals, but resorcinol can be, and its axial ratio $a : b$ was found to be very like that of benzene, while the ratio $c : b$ was considerably different, the ratios found being $a : b : c = 0.910 : 1 : 0.540$. Next, turning to the three nitro-derivatives of phenol, orthonitrophenol $\text{C}_6\text{H}_4(\text{OH})(\text{NO}_2)$, dinitrophenol $\text{C}_6\text{H}_3(\text{OH})(\text{NO}_2)_2$, and trinitrophenol $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$, he found them all to crystallise likewise in the rhombic system, their respective axial ratios $a : b : c$ being $0.873 : 1 : 0.60$, $0.933 : 1 : 0.753$, and $0.937 : 1 : 0.974$. The $c : b$ ratio is different for the first two, but the values of the $a : b$ ratio are remarkably similar to those of benzene.

He then studied the nitrobenzenes, meta-dinitrobenzene $C_6H_4(NO_2)_2$ and trinitrobenzene $C_6H_3(NO_2)_3$, and found similar relations as regards the ratio $a : b$, to benzene, the actual axial ratios being $0.943 : 1 : 0.538$ and $0.954 : 1 : 0.733$ respectively. It is noteworthy, however, that if the ortho-isomer of meta-dinitrobenzene be studied it is found that the symmetry has become lowered to monoclinic. Indeed, for instance, the replacement of hydrogen by chlorine or bromine, or by a CH_3 group, was almost generally found to produce so much more change that the system was lowered to monoclinic. Yet even in these cases the prism zone angles remained very similar, the angle between the primary prism faces (110) and $(1\bar{1}0)$ not varying more than three to five degrees. So that even although the crystal system be altered (usually lowered), yet there is a striking amount of similarity in the angles of some dominant zone, the primary prism zone in the cases above mentioned, the change due to replacement of hydrogen by a halogen or a radicle then being chiefly manifested by a lengthening or shortening of this zone axis, the crystal-axis c .

Hence the work of von Groth established the fact of the phenomenon of isogonism, to which he gave the term "morphotropy." It is a phenomenon which must not, however, be confounded at all with isomorphism, even although isomorphism may be considered as morphotropism or isogonism over all the zones. For very great care has to be taken with these complicated organic compounds, which are subject so largely to the possibility of chemical isomerism. In the case of the aromatic compounds, the derivatives of benzene, the ortho-, meta-, and para-isomers, according as the hydrogen atoms in benzene are replaced by two radicles at adjacent, alternate, or opposite positions of the hexagonal benzene ring of six CH groups, crystallise differently, often completely so.

Von Groth returned to this subject in 1904, after the principle of using molecular volumes and topic axial

ratios as relative measures of the space-lattice unit cells had been thoroughly established for the cases of substances having space-lattices constructed on the same plan of symmetry. This 1904 research was directed to cases of similar types of replacement, in which the plan of symmetry might be expected to be the same. Ammonium iodide NH_4I and its homologously substituted alkyl derivatives, $\text{N}(\text{CH}_3)_4\text{I}$, $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$, and $\text{N}(\text{C}_3\text{H}_7)_4\text{I}$, were especially studied. Ammonium iodide is cubic, with cube cleavage, the space-lattice being that of the simple cube. The specific gravity of the crystals is 2.501, the molecular weight 143.83, and V the molecular volume is consequently 57.51. The topic axial value $\chi = \psi = \omega = \sqrt[3]{V}$ works out as 3.860, the relative measure of the unit cell edges. Tetra-methyl and tetra-ethyl ammonium iodides crystallise in the tetragonal system, the former with perfect cleavage corresponding to cubic, that is, parallel to $\{100\}$ and $\{001\}$, the two forms of four and two faces analogous to the six cube faces. But the c -axis is now shorter relatively to the two lateral equal axes a and b , the reality as indicated by the topic axial ratios χ and ψ apparently being that the lateral axes both equally enlarge while the vertical axis ω remains almost the same. On replacing methyl by ethyl the cleavage is upset, but the molecular volume and the lateral topic axes again increase more or less regularly, while ω for the vertical axis remains still constant. The propyl compound, however, indicates relatively much more change, the symmetry itself being upset, a difference becoming manifest in the two lateral axes, the crystal thus becoming rhombic, and the vertical axis also elongated.

Vegard, in 1917, however, carried out the X-ray analysis of this group of substances, and found that the structures do not remain the same, and thus, as topic axial ratios can only safely be relied on for valid comparisons when the structures are of the same type, he assumed that the interesting conclusions of von Groth must be accepted

with reserve. It may be, however, that further work is necessary to settle the matter conclusively.

Polymorphism.—The fact that certain substances crystallise in more than one form was first established by Mitscherlich in 1821 and following years, as described in Chapter II, for the cases of sodium di-hydrogen phosphate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (rhombic pyramidal and rhombic bi-pyramidal), calcium carbonate CaCO_3 (trigonal calcite and rhombic aragonite), the sulphates (rhombic and monoclinic) of magnesium, zinc, nickel, iron, and cobalt $\text{M}'\text{SO}_4 \cdot 7\text{H}_2\text{O}$, mercuric iodide HgI_2 (red tetragonal and yellow rhombic), and the element sulphur (rhombic and monoclinic). As all these substances exhibited two different forms he gave to the phenomenon the name “dimorphism.”

Since the time of Mitscherlich many other dimorphous substances have been discovered, and some which are trimorphous and one or two tetramorphous, so that the property is best referred to as “polymorphism.” Indeed, with the growth of organic chemistry a very large number of supposed cases of polymorphism have been described, but eventually have mostly turned out to be cases of chemical isomerism, truly different substances of the same empirical composition but of quite different chemical constitution.

The best-known instance of trimorphism is that of the dioxide of titanium, TiO_2 , which occurs naturally in two quite different tetragonal minerals, anatase and rutile, and in a rhombic form, brookite, a substance famous for exhibiting crossed-axial-plane dispersion of the optic axes. Ammonium nitrate, NH_4NO_3 , is, according to Lehmann, a tetramorphous substance, within temperature limits up to its melting point 168°C . When the salt is fused, it first resolidifies in isotropic (cubic) crystals, usually of a skeletal nature. On coming down to 125° , the mass becomes doubly refractive, and rhombohedral crystals

are obtained from a saturated solution at this temperature. Again cooling further, at 83° rhombic needles are produced, and once more at 32° another change occurs to a fresh rhombic form. It is this last-mentioned rhombic form which is obtained in large crystals by the evaporation of an aqueous solution at the ordinary temperature. Each transition is accompanied by a change in density, and in specific heat. The ordinary low temperature form, which is usually acicular although occasionally obtained in good crystals of a tabular character, is distinguished by remarkable plasticity. The long crystals can be bent without fracture into an angle shape, or even into a loop if the operation be slowly performed; but if suddenly bent they break, the crystals being not only plastic but brittle, the bending not being due to viscous flow but to plasticity, accompanied by some elasticity, as the crystal unbends somewhat on removal of the bending force.

Mercuric iodide, HgI_2 , is one of the most interesting cases of dimorphism. From aqueous solutions the salt separates in red tetragonal crystals; but if it be fused, the crystals obtained on cooling are yellow rhombic ones, and the same are obtained on volatilisation and sublimation. If a solid body be held in the vapour, the body having been previously rubbed in one part with red crystals and on another part with yellow crystals, that same variety is deposited on the part. The critical temperature of the change is 126°C . If the yellow crystals are kept undisturbed they persist for a long time, but if they are scratched or struck they become immediately converted into the red tetragonal form. Thermal and volume changes accompany the change of form from one variety into the other.

Sodium monophosphate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, can be obtained from metastable solutions in either of its two forms, according to the temperature of the solution; if the latter be warm the ordinary rhombic variety is produced, whereas if it be very cold the second rhombic variety is deposited.

Calcium carbonate, CaCO_3 , is not only found naturally in the well-known trigonal-rhombohedral form of calcite and the rhombic form of aragonite, but may be obtained from solution in carbonic acid, or by precipitation of a very dilute solution of calcium chloride by a soluble carbonate, in either form according to the temperature. If the solution is below 30°C. , or the precipitation is performed with cold solutions, the calcite form is obtained in minute rhombohedra; but if the temperature be over 70° the

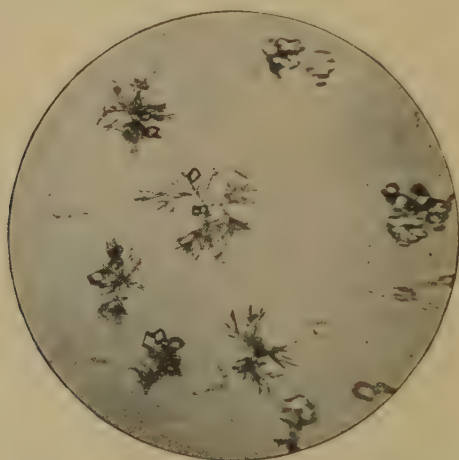


FIG. 51.—The Two Forms of CaCO_3 precipitated from a moderately hot Solution.

feathery, rapid crystallisation form of aragonite is alone precipitated; or if the temperature lie between 30° and 70° a few miniature rhombs of calcite are to be seen among the feathery tufts of aragonite. A photomicrograph of such a case is reproduced in Fig. 51. It has been shown that aragonite changes into calcite at rates which increase with the temperature, and is almost instantaneous at 470°C. The change is pseudomorphous, that is, the interior is converted to the structure of calcite, but the external form remains apparently unaltered, that of the original aragonite crystal.

The dimorphism of antimony oxide, Sb_2O_3 , is a case readily demonstrated. If a little of the oxide be heated in a test tube, and a microscope glass slip be held over the mouth, crystals of the substance are deposited by sublimation on it. These crystals are of two very distinct forms, long sharp needles of the rhombic form, and octahedra of the cubic form, which are often perched on the needles. A photomicrograph is reproduced in Fig. 52.

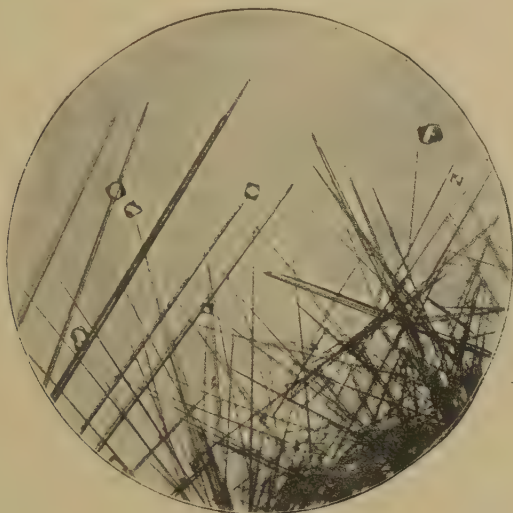


FIG. 52.—The Two Forms of Antimony Oxide.

Temperature, then, is obviously a prime factor determinative of the form in the cases of polymorphous substances, and as a general principle it may be considered that each form has its life-range of temperature. Consequently, at the ordinary temperature one form is stable and the other unstable. Yet it is a very remarkable fact that it is not possible to state with complete truth that sooner or later the unstable form will always break down; for there are notable instances—such as aragonite, which is found in nature in beautiful crystals of considerable size which have probably persisted for many ages of

time—in which the unstable form, in this case of carbonate of lime, may be preserved for long periods without apparent change. It would appear to be probable that such a substance forms both space-lattices with almost the same facility, some very slight cause, the temperature of a hot or a cold day for instance, being responsible for which particular one is developed. For it may happen that the transition point is one of the degrees of temperature included in the meaning of the common phrase “ordinary temperature,” or very close thereto. Also the phenomenon of persistence, akin to superfusion or metastable supersaturation, may be operating. From all these considerations it will be clear that it is unwise and incorrect to lay down hard and fast rules for, or explanations of, polymorphism. The facts in each case are best merely recorded, with great care and detail, for each case studied.

A clear case, however, where there is no difficulty, is that of the element sulphur. The ordinary rhombic form of sulphur, found near volcanic vents in excellent and often large crystals, or deposited from solution in carbon bisulphide, CS_2 , is quite stable up to 95.6°C ., when the monoclinic variety attempts to form, with absorption of heat. If not disturbed, and no monoclinic form be produced, the substance melts at 113.5° ; but if any monoclinic form be present no melting occurs until the temperature of 119.6° be reached, 6° higher. If the melt be allowed to cool, as is well known, the monoclinic form alone separates, in long needles, and can be isolated by pouring out the remaining liquid, when one half of it has solidified in the crystals. If the operation occur in a crucible which is then immediately efficiently closed, so that no germ-crystals of rhombic sulphur can settle on them from the air, the monoclinic needles can be preserved at the ordinary temperature for a short time. Very soon, however, next day as a rule, spontaneous breaking down of the needles begins to occur, into a powder of minute rhombic crystals,

and proceeds fairly rapidly to completion. Moreover, if cooling liquid sulphur in a very clean crucible be allowed to rest quietly for a few minutes, and its surface be then touched with a rhombic crystal, the crystallisation which shortly begins is that of the rhombic form, and occurs with great rapidity until the whole is a mass of rhombic crystals. This case of sulphur is thus clearly one of those in which the two forms have their own distinct limits of temperature, and the critical limit of 95.6° is well removed from the ordinary temperature.

The case of carbon, however, the other common element which exhibits two distinct forms, diamond and graphite, would appear to be quite different. For both diamond, the hardest substance known, and brilliantly transparent, and graphite, perhaps the softest, minutely flaking into a lubricating opaque powder, are wonderfully stable at the ordinary temperature. Moreover, the very thorough study of these substances which has been made by means of X-rays, by Sir William Bragg, Debye and Scherrer, Hull, Hassel and Mark, and Bernal has shown that the cubic structure of diamond is such that each carbon atom is surrounded by four others tetrahedrally arranged, while that of graphite can be readily derived from it, and is hexagonal, consisting of flat layers of hexagonal rings of carbon atoms separated by a comparatively large distance. A sphere can be surrounded in close packing by twelve other similar spheres, and if the attraction between two atoms could be represented by a central force only they would attract their twelve neighbours; but the carbon atom shows no attraction for more than four, so the forces between two carbon atoms cannot be only central. The hardness and rigidity of diamond indicate that the forces are oriented, and along four lines drawn from the centre of a tetrahedron to its corners, and that there is great resistance to change along these directions. Hence the carbon atom behaves as if it had a structure of a tetrahedral nature,

and as this agrees with its chemical characters, which are known to be a function of the outer electrons of the atomic structure, it is likely that there is something of a tetrahedral character about the arrangement of the electrons of the outer shell, or their mean positions if in orbital motion.

The unit cell of graphite is shown in Fig. 53, and is of hexagonal type and contains four atoms. The dimensions are 6.8 \AA.U. for the c -edges and 2.45 for the a -edges, the axial ratio $c : a$ being 2.77 . Repetition of the cell pro-



FIG. 53.—Space-Lattice Cell of Graphite.

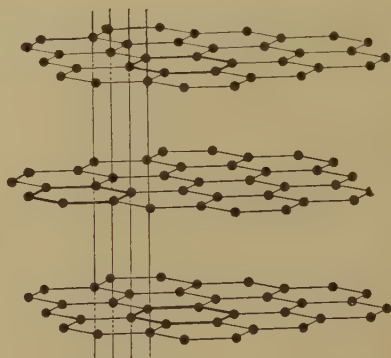


FIG. 54.—Structure of Graphite.

duces the structure of flat hexagonal rings of carbon atoms shown in Fig. 54, separated by the comparatively large distance 3.4 \AA.U. The distance of closest approach of the carbon atoms in the hexagons is 1.43 \AA.U. , as compared with 1.54 \AA.U. in diamond. The symmetry of the complete structure is apparently hexagonal holohedral, D_{6h}^3 . Bohr's earlier carbon atom, with four 2_1 orbits arranged tetrahedrally, thus corresponds to the diamond, and his later suggestion of three 2_1 orbits and one 2_2 orbit is more suitable for graphite. The unique fourth electron, which is thus characteristic of and is apparently so loose in graphite, is likely to be also the cause of the metallic-like properties

which distinguish graphite, and of the great difficulty experienced in converting it into diamond.

The diamond structure, shown by the model represented in Fig. 55, is that of the face-centred cube with a carbon atom also at the centre of each of the four alternate cubelets of the eight which make up the face-centred cube, and in which the four outer electrons of each atom are of equal value and arranged apparently tetrahedrally; it may be converted to that of graphite by elongating the vertical distances or bond shown in Fig. 55, between the pairs of atoms standing vertically over one another in the figure, while at the same time giving some rotation to the three

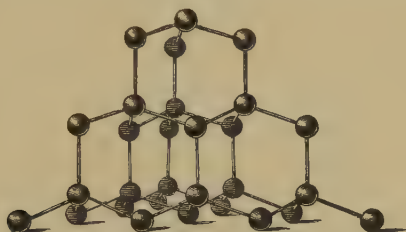


FIG. 55.—Model of Diamond Structure.

others lying in the horizontal plane, relatively to those in the next layer. The rings formed by the horizontal layers in the diamond, which likewise make up hexagons, are puckered, whereas the work of Hassel and Mark and of Bernal would indicate flat unpuckered hexagonal rings in the case of graphite.


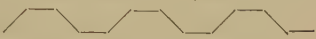
Whether the hexagonal rings of graphite be puckered or flat does not seem to matter much chemically, or even geometrically. In either case they correspond to the hexagonal ring of benzene and the aromatic compounds in general, while the carbon of the fatty series would appear to be as in the diamond.

It is highly interesting that these two structures of carbon, found in diamond and graphite respectively, should thus persist in the two great divisions of organic compounds, the diamond structure in the chains of the

aliphatic series, and the graphite structure in the hexagonal rings of the aromatic series of carbon compounds. Indeed the stability of both forms of carbon is truly remarkable.

This case of the two varieties of carbon has been considered as one of allotropy, on the same principle as that of ozone, where the free gaseous molecule consists of three atoms of oxygen, instead of the two-atom molecule of ordinary gaseous oxygen. But it would appear to be quite unnecessary to assume this kind of thing in the case of the solid element carbon, the two structures of diamond and graphite—built up of carbon atoms simply differing in the disposition of the four electrons of the outer shell and their type of orbit, in the one case similar and symmetrically tetrahedrally arranged, but in the other in three similar orbits and one dissimilar orbit—themselves affording full and adequate explanation of the two different varieties of the element. It is thus unnecessary to look for molecules composed of a different number of atoms, as no such molecules can be recognised. It is possible that a similar explanation will some day be forthcoming for the two so-called allotropic varieties, yellow and red, of the element phosphorus.

The connection of the diamond structure of carbon with that of the aliphatic division of the organic compounds is interestingly brought out by some work in Sir William Bragg's laboratory at the Royal Institution by Müller and Shearer, on the long-chain molecules of the solid or waxy fatty acids and homologous hydrocarbons. When pressed on to a flat surface they form flaky crystals in which by X-rays it is readily possible to determine the spacing, that is the thickness of the monomolecular layer. The molecules appear to have their lengths perpendicular to the layer. If one thus studies the successive homologues in the series, differing by CH_2 at each step, they are found to show a regular increase in the thickness of this layer, which has been found to be of two values, 2 Å.U. and 2.5 Å.U., for every

two atoms added. If the carbon atoms are attached as in the diamond, at their usual distances of 1.54 \AA.U. , and two successive attachments occur at the angle between two of the lines joining the centre of a tetrahedron to its corners, the distance between two successive pairs of carbon atoms would be exactly 2.5 \AA.U. for the simplest linear zig-zag arrangement in one plane, , and 2.05 \AA.U. if the arrangement were thus: . Hence, it is concluded that in these chain compounds the linkage is on the diamond plan, and in one of these two forms of zig-zag. It is also found that the length of the zig-zag chain remains the same whatever be the nature of the side or end attachments, whether they be simply two side-hydrogens or replacing radicles or oxygens, to each carbon atom, as in the fully saturated series, or whether two or four hydrogens are removed, leaving the two carbon atoms doubly or triply linked together. It is then simply like stripping opposite pairs of leaves from the stem of a plant. In the case of the fatty acids, which have an active group COOH at the end of the chain, the chain doubles when action occurs, the two chains joining end to end, with the active groups in the middle, and the result is like two sticks joined into one.

The occurrence of the graphite structure in the aromatic division of organic compounds has been rendered very plain by the X-ray analyses of naphthalene and anthracene and their derivatives. Benzene itself, the simplest of the ring compounds, being a liquid and requiring to be frozen in order to get crystals, does not lend itself readily to X-ray analysis. Several attempts, however, have been made to determine its structure, and the latest, by H. Mark, by the rotating crystal method, indicates rhombic bipyramidal symmetry, rhombic holohedral class 8, with four molecules of C_6H_6 to the unit cell of the space-lattice, and axial or cell-edge dimensions of 6.9 , 9.7 , and 7.4 \AA.U. But the two-ring naphthalene C_{10}H_8 and the three-ring anthracene

$C_{14}H_{10}$ crystallise well enough, in spite of flakiness, to enable a thorough study to be made by means of X-rays. The results show that the space-lattice unit cell of each of these substances contains two chemical molecules, arranged with their long axes parallel to each other, and as the mirror-reflection of each other across the single plane of symmetry which these monoclinic crystals possess. In each flake the molecules do not stand perpendicularly to the plane of the flake, but lean over like the wind-blown wheat in a cornfield. The ratio of the lengths corresponds exactly to a two-benzene-ring molecule for naphthalene, and a three-ring molecule for anthracene. In these ring compounds the carbon atom has the same characteristics as in graphite, or as in diamond with one of the valencies unused or but feebly used. The measurements with naphthalene derivatives (acenaphthene and the β -naphthols), and other ring-compounds, confirm these conclusions in every way.

Distinction between Polymorphs and Isomers.—Truly polymorphous substances thus only differ in their crystal structure and the properties dependent thereon. On fusion, volatilisation, or solution in a solvent, they afford absolutely identical chemical molecules in the liquid or gaseous state. Consequently, in doubtful cases, the test is, do the two substances yield these identically similar molecules, or do they afford different ones? If the latter, then the two substances must have been chemical isomers, two different chemical substances, and not polymorphous forms of the same chemical substance. A correct diagnosis, however, is sometimes rendered difficult by the fact that not infrequently chemical isomers are readily converted one into the other by heat, and in the cases of tautomeric (so readily convertible as to be distinguished with difficulty) isomers, even by solution. Hence, great discrimination and careful observation have to be exercised.

A very ingenious method for discriminating between

isomers and polymorphs has been devised by Sidgwick. If two isomers are dissolved in a solvent, being different chemical substances they dissolve independently without appreciable mutual interference, each according to its own solubility; so that if a quantity of the less soluble be added to a saturated solution of the more soluble isomer an increase of concentration occurs. But if the two substances thus treated be polymorphs, there will not only be no increase but actually a decrease of concentration; for on solution polymorphs give the identically similar chemical molecules. The Beckmann process of determining the depression of the freezing point of the solvent by the two solids is used in actual practice, first when added separately and then together. If the two solids are polymorphs of the same chemical molecules the cryohydric point for their mixture is intermediate between the cryohydric points of the two when added separately. But if they are isomers the cryohydric point is below that for the more soluble solid.

Polysymmetry.—A peculiar kind of isomorphism, to which the term polysymmetry has been given in order to distinguish it from ordinary polymorphism, is displayed by certain substances which closely simulate a higher symmetry than they really possess, and which pass over into that higher symmetry at some definite temperature. One of the best examples is potassium sulphate, the orthorhombic crystals of which have been shown by the author to exhibit a primary prism angle $ap = (100) : (110)$ of $29^\circ 48'$, only $12'$ short of 30° . Moreover, it is frequently triply twinned, so as to resemble a very short hexagonal prism doubly terminated by hexagonal pyramids, as shown in Fig. 56; so that were it not for a very low, almost imperceptible, ridge running from tip to tip of the double pyramid, along the middle of each face, the crystal might well be taken for a truly hexagonal or trigonal one. Now the interesting point is, as first shown by Mallard, that if

the crystal be heated to between 600° and 650° C. a sudden change occurs into the truly hexagonal form, the 12 minutes of difference disappearing and uniaxial optical characters being developed instead of biaxial. The exact temperature was afterwards given by Le Chatelier as 580° on heating and 530° on cooling; also still more recently by Hüttner and Tammann, Kurnakow, and Nacken, as 587° , 610° , and 595° respectively, the singular phenomenon having been confirmed by all these workers.

A double sulphate of sodium and potassium, $\text{NaK}_3(\text{SO}_4)_2$, and an analogous chromate, $\text{NaK}_3(\text{CrO}_4)_2$, which crystallise

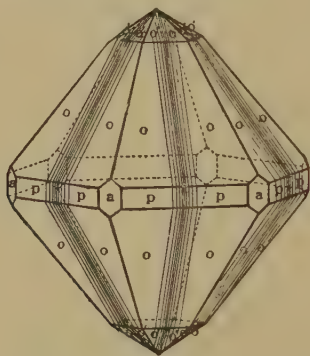


FIG. 56.—Triplet of Potassium Sulphate.

in the monoclinic system but with a closely hexagonal habit, have been shown by Gossner to exhibit similar behaviour, becoming converted into a truly hexagonal form on heating.

Quartz, SiO_2 , is also one of the substances exhibiting two polysymmetric forms, which are known as α - and β -quartz. But the second variety, β -quartz, has the same appearance and transparency, that of the same trigonal trapezohedral class-18 symmetry as ordinary α -quartz, although according to Friedel the etch-figures no longer correspond to this class, but to hexagonal symmetry; also the optical activity remains the same, but there is a complete change in regard to certain other physical properties,

such as rate of change of density with temperature. The temperature of conversion was given as 570° by Le Chatelier, and 600° by Friedel. More recently F. E. Wright has studied the variation of the angle between the rhombohedron and prism faces of quartz, and found it to change eleven minutes between 0° and 575° C. At this temperature the curve, hitherto quite regular, shows a marked discontinuity, and the signal images from the rhombohedron and prism faces became first blurred, then again sharp and clear but shifted considerably, due to the change from the α -variety to the β -form.

Silica, SiO_2 , crystallises in no less than four different forms, three of which, cristobalite, tridymite, and quartz, are polysymmetric, each having an α and β variety. The fourth, quartzine, is a fibrous form, which is the same as chalcedony when the fibrous nature is almost submicroscopic, but when best developed shows the fibres as minute triclinic needles. Above 1470° C. the other forms become converted into cristobalite; between 870° and 1470° tridymite is stable, and quartz heated to this temperature passes into it; below 870° quartz is the stable form.

The ordinary α -form of cristobalite is tetragonal, with pseudo-cubic habit, resembling octahedra but really tetragonal pyramids. At 175° these crystals pass into a truly cubic octahedral form, that of the β -variety.

The ordinary α -variety of tridymite, that present for instance in meteorites (in which quartz never occurs), is rhombic, with pseudo-hexagonal habit and angles very close to hexagonal. At temperatures varying according to different observers from 130° to 160° it becomes suddenly converted into the truly hexagonal β -variety.

The two varieties of quartz, α and β , have already been described, and further details from recent researches will be found on pages 192 to 195.

As regards quartzine, Wallerant succeeded in determining the optic axial angle ($2V_a$) to be 58° , and the refractive

indices to be $\alpha = 1.5325$, $\beta = 1.5355$, and $\gamma = 1.5435$; and Sohncke, using these data, in the year 1876 suggested that quartz may be really formed of quartzine layers, spirally arranged like the mica films of Reusch, and has calculated that the refractive indices of quartz on this supposition should be about 1.543 and 1.553. Now the actual indices of quartz are $\omega = 1.5443$ and $\varepsilon = 1.5534$, extraordinarily close to Sohncke's calculated values. It thus appears that when the conversion change occurs at 575° the artificial trigonal trapezohedral, class-18, quartz constructed out of spirally arranged quartzine layers becomes converted to a real entity, β -quartz, or more correctly "real" quartz on this assumption regarding quartzine, of the same class-18 symmetry. The alternative, which is indicated by some of the observations, such as those of Friedel with the etch figures, is that true quartz, the α -variety, is converted at 575° into a hexagonal trapezohedral, class-24, β -variety. Which alternative is the truth remains to be decided by further work, and Sir William Bragg's new X-ray investigation appears to offer the desired solution. (See page 195.)

Isomorphism of Polymorphous Substances.—It usually happens that if a dimorphous substance is a member of an isomorphous series, other members, if not all, are also analogously dimorphous, and are then said to be "isodimorphous." One of the first known and most interesting cases is that of the metallic sulphates known as the "vitriols," referred to already on page 39. The Epsom salts group, composed of the sulphates of magnesium ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), zinc ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), and nickel ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) are normally rhombic, while the usual form of the sulphates of ferrous iron ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and cobalt ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) is monoclinic. But if a crystal of one of the salts of the rhombic group be dropped into a metastably supersaturated solution of a member of the monoclinic group that member will crystallise in the rhombic form, in crystals isomorphous with the Epsom salts group; and

conversely, if a monoclinic crystal of the second group be dropped into a solution of a member of the rhombic group that member will be deposited in monoclinic crystals. Both groups are dimorphous in common, but the temperature limits of the five different salts are such that for the ordinary temperature the stabler form of the sulphates of magnesium, zinc, and nickel is the rhombic one, while for ferrous and cobaltous sulphates it is the monoclinic form which is the stabler of the two and therefore commonly produced at ordinary temperatures.

Another case, which has come under the author's own observation, is one consisting of three (then new and measured for the first time) homologous organic compounds (differing by increments of CH_2), the methyl CH_3 , ethyl C_2H_5 , and propyl C_3H_7 derivatives of the substance triphenylpyrrholone. Each of the three compounds is dimorphous, and possibly trimorphous, but only two forms of each are readily prepared, the only different conditions being those of temperature, the solvent being the same. The methyl compound crystallises in trigonal rhombohedra and in triclinic prisms. The ethyl compound forms triclinic crystals showing the same "forms" as the methyl compound, and with faces inclined at angles which only differ on the average (of 23 measured angles) by $2^\circ 19'$ and in the maximum by $4^\circ 34'$, the isomorphism being complete for all the zones, the crystals not being merely morphotropically isogonal. The ethyl derivative deposits monoclinic crystals for its second form, and they are very interesting optically, for they exhibit crossed-axial-plane dispersion of the optic axes at the ordinary temperature, the uniaxial figure being produced for greenish yellow light of the wave-length 0.000575 mm. The ethyl compound also has a rhombic third form, but this is very fugitive. The propyl compound affords a monoclinic form resembling almost identically that of the ethyl compound, the same "forms" being present with faces inclined at similar angles

and completely isomorphous, the crystals not being merely isogonal. The propyl monoclinic crystals also exhibit large dispersion of the optic axes like the ethyl monoclinic crystals, but not quite enough to extend over one plane. The angular differences between these two monoclinic forms of the ethyl and propyl compounds are on the average (of 22 angles measured) $1^{\circ} 53'$, and the maximum $3^{\circ} 42'$. Lastly, the propyl derivative also affords a rhombic variety, isomorphous with the fugitive rhombic form of the ethyl compound. These three substances thus afford an example of the close isomorphism of CH_2 homologues, of isomorphism in pairs, and of isodimorphism in the case of the ethyl and propyl compounds, the temperature limits for stability not permitting all three compounds to have one of the forms in common. Indeed the three may be considered as isopolymorphous, the forms actually obtainable of all the possible forms being those permitted by the temperature limits of the various varieties for each of the three substances.

CHAPTER IX

ENANTIOMORPHISM AND OPTICAL ACTIVITY. QUARTZ AS TYPICAL EXAMPLE

ELEVEN of the 32 classes of crystals possess no plane of symmetry, and are in consequence characterised by the possibility of right- or left-handedness, as regards the development and disposition of "forms" of faces other than the primary. A single crystal of any one of these eleven classes showing forms other than the primary, when reflected in a plane mirror, affords an image similarly symmetrical and with identically similar angles, but laterally inverted. Both forms of the crystal, right- or left-handed, may and do usually exist, and neither can be brought to look like the other either by rotation or otherwise; they are therefore said to be "ENANTIOMORPHOUS," from *ἐναντίος*, opposite, and *μορφή*, shape. Now the whole of the substances which in their crystals have been observed to display the phenomenon of optical activity, that is, the crystals of which are capable of rotating the plane of polarisation of a beam of plane-polarised light, to the right or to the left (clockwise or anticlockwise), have been found to produce crystals which belong to one or other of these eleven classes of crystals, and to display enantiomorphism when their facial development extends to other than the primary faces. It does not necessarily follow, however, and it is not a fact, that all crystals possessing the symmetry of one of these enantiomorphous classes exhibit optical activity; barium nitrate (cubic class 28) is such an instance of inactivity. Indeed it is only such of them as possess a screw structure, one or more screw axes, that do so; for optical rotation in the case of

solids appears to be caused by such screw structure, which can, of course, be right- or left-handed. The great majority do possess such a screw structure, however, for it is very naturally a feature of most cases of enantiomorphism.

The phenomenon of rotatory polarisation of light is, of course, well known to be displayed by many organic liquids and by the solutions of many organic substances in solvents. In these cases it is obviously the chemical molecules themselves that are enantiomorphous, that is, occur in one or both of two kinds, the stereometric arrangement of the atoms in these two varieties being the mirror-images of each other. Moreover, such molecules are very likely to give rise to enantiomorphous crystal structures, the screw-like arrangement being a very natural one for them to take up on building themselves up into the solid crystal edifice. Hence, most of the optically active substances are so both in the solid crystalline and the liquid or dissolved condition. But there are some notable exceptions, sodium chlorate, NaClO_3 , for instance, in which the crystal alone is optically active, the molecules themselves not being enantiomorphously constituted. The substance in the liquid or dissolved condition, in which the molecules are free to roll about and thus build up no structure, is therefore optically inactive. In these cases the optical activity is the result of the particular point-system or space-group which is developed on crystallising being one causing optical rotation.

The following are the *Eleven Enantiomorphous Classes*, with examples where such are definitely established, and their angle of rotation for sodium light and for a plate one millimetre thick.

CUBIC SYSTEM.—*Class 29, Pentagonal Icositetrahedral Class.*—No well-established rotatory example.

Class 28, Tetrahedral Pentagonal Dodecahedral Class.
—Example, sodium chlorate, NaClO_3 , $3^\circ 8'$.

HEXAGONAL SYSTEM.—*Class 24, Hexagonal Trapezohedral Class.*—Example, β -quartz.

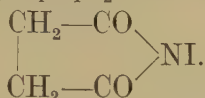
Class 23, Hexagonal Pyramidal Class.—Example, potassium lithium sulphate, KLiSO_4 , $3^\circ 26'$.

TRIGONAL SYSTEM.—*Class 18, Trigonal Trapezohedral Class.*—Example, quartz (ordinary α -), SiO_2 , $21^\circ 44'$.

Class 16, Trigonal Pyramidal Class.—Example, sodium periodate, $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$, $23^\circ 18'$.

TETRAGONAL SYSTEM.—*Class 11, Tetragonal Trapezohedral Class.*—Example, strychnine sulphate, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $13^\circ 15'$.

Class 9, Tetragonal Pyramidal Class.—Example, iodo-succinimide, $\text{C}_4\text{H}_4\text{O}_2\text{NI}$. Constitution



ORTHORHOMBIC SYSTEM.—*Class 6, Rhombic Bispfenoidal Class.*—Examples, Seignette salts, (a) sodium potassium dextro-tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (Rochelle salt), dextro-rotation for each optic axial direction $+1^\circ 21'$; (b) sodium ammonium dextro-tartrate, $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, lævo-rotation for each optic axis $-1^\circ 33'$; the solutions of both salts are dextro-rotatory.* Epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, for each optic axis $+2^\circ 36'$. Sodium dihydrogen phosphate, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $-4^\circ 27'$.

MONOCLINIC SYSTEM.—*Class 4, Monoclinic Sphenoidal Class.* Examples, (a) Tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$, the ordinary dextro variety (dextro in solution). Plane of optic axes perpendicular to symmetry plane, so rotations along two optic axes are equal, namely, $-11^\circ 24'$. (b) Cane-sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. Plane of optic axes is the symmetry plane, so rotations along two optic axes are unequal and of different sign,

* Dufet obtained for the NaK Salt $+1.35^\circ$ instead of Pocklington's 1.2° ; and for the NaNH_4 salt -1.55° instead of Pocklington's 1.51° (Dufet, *Zeitschr. für Kryst.*, 1907, **42**, 194).

namely, $-2^{\circ} 12'$ and $+6^{\circ} 24'$. (c) Rhamnose, optic axes also in symmetry plane, hence two axes different, $-12^{\circ} 54'$ and $-5^{\circ} 24'$. (Dufet, *Zeitschr. für Kryst.*, 1907, 42, 195).

TRICLINIC SYSTEM.—*Class 1, Asymmetric Class.*
No example studied.

It is thus one of the most important facts of chemical crystallography that almost every chemical substance the molecules of which in the liquid, dissolved, or solid crystalline condition rotate the plane of polarised light, to the right or to the left, crystallises in one of the above eleven classes of only axial symmetry, and forms two varieties of crystals which are the mirror images of each other, but which, if they develop other than primary forms, are not themselves identical with their own mirror-images, and which also rotate the plane of polarisation to the right or left when the light passes along the optic axis if uniaxial, or along the two optic axes if biaxial, or in any direction if the crystal be isotropic, of cubic symmetry.

Section-plates perpendicular to the single optic axis if uniaxial, or to one or both of the two optic axes if biaxial, or cut in any position if isotropic (the rotation being equal in all directions), usually require to be relatively thick in order to exhibit optical rotation satisfactorily. Thus, for quartz, a convenient thickness of plate for the study of the colour phenomena is about $7\frac{1}{2}$ millimetres. The reason why in doubly refractive crystals it is necessary to study the phenomenon of optical rotation with a plate perpendicular to an optic axis is that it is only along this direction that the colour phenomena of double refraction in polarised light are eliminated; and also because the circular polarisation orbits rapidly become converted into elliptical, as the axis is departed from, and eventually, with a plate parallel to the optic axis, become truly linear.

It is consequently easiest to produce and study the pure

phenomena of optical rotation with parallel surfaced section-plates or tabular crystals belonging to the cubic system, or with plates cut truly perpendicularly to the single optic axis, direction of no double refraction, of a tetragonal, hexagonal, or trigonal crystal. Consequently, the greater amount of observations on optical rotation in the solid state have been made with crystals belonging to these four systems of higher symmetry. With biaxial crystals it is necessary to cut two plates in each case, one perpendicular to each of the two optic axes. Moreover, these directions are not so perfectly directions of no double refraction. In the case of crystals belonging to the rhombic system, the two optic axes will always show like amounts and sign of rotation, by reason of their symmetrical positions with respect to a principal axis of the optical ellipsoid, which is always also a crystal axis. In the monoclinic system this is only true when the plane of the optic axes is perpendicular to the single plane of symmetry, as in the case of tartaric acid; if the two optic axes lie in the plane of symmetry, the amounts of rotation which they display are different, and often considerably so, as in the cases of cane sugar and rhamnose. Also the signs may be different for the two axes, as in the case of cane-sugar. The conditions in the triclinic system are extremely complex, and the two optic axes always show unequal amounts of rotation. There is also much more difficulty in the study of the rotation of biaxial crystals; for instead of the whole field being evenly coloured, in the dark field of the polariscope between crossed Nicols, as in the case of uniaxial crystals, it is only the hyperbolic brush vertices that can be examined for colour instead of blackness.

One advantage, however, in the study of the optical rotation of solids as compared with that of liquids, is that solid crystals usually rotate far more powerfully than liquids. Thus for instance, while a plate of quartz one millimetre in thickness rotates the plane of polarisation of

sodium yellow light for 21.73° , a layer of turpentine of the same thickness (1 mm.) rotates the same radiation to the left for only 0.296° ; and a layer also of 1 mm. of a fifty per cent. aqueous solution of cane sugar rotates it for only 0.336° to the right. The temperature of 20°C. is taken as the standard temperature for the determination of rotation, and the figures quoted correspond to that temperature. Liquids can be mixed with an inactive miscible liquid without losing their rotatory power, and, as already shown many optically active crystals may be dissolved in water or other solvent and their solution will show optical rotation, as in the case of cane sugar, the enantiomorphism being not only that of the crystal structure but that of the free molecules themselves. But the amount of rotation, and its sign, may be different.

Quartz as typical Example of Optically Active Substance.—The very best possible active crystallised substance for study as a typical example is quartz, SiO_2 . For it has the double advantage of being optically uniaxial, being of class-18 trigonal trapezohedral symmetry, one of the eleven enantiomorphous classes, and of being a beautifully transparent colourless substance obtainable in large crystals of great hardness (7 in Mohs' scale) and durability and without any facility for cleavage, the cleavage along the rhombohedral planes $R\{100\}$ being so imperfect as rarely to be seen or produced by working, and not at all interfering with the preparation, by cutting, grinding, and polishing, of flawless section-plates perpendicular to the optic axis.

Two typical right- and left-handed quartz crystals are shown in the accompanying Fig. 57.

They are characterised by the little faces of the right trigonal pyramid of the second order $s\{41\bar{2}\}$, and of the right positive trapezohedron $x\{4\bar{1}2\}$ on right-handed crystals, which are also right-handedly (dextrogyrate) optically active, and of the complementary left trigonal

second order pyramid $s\{4\bar{2}1\}$ and the left positive trigonal trapezohedron $x\{4\bar{2}\bar{1}\}$ on left-handed crystals, which are also lævograte optically. The other faces present are the hexagonal prism of the first order $m\{2\bar{1}\bar{1}\}$, which is common to the trigonal and hexagonal systems, the primary direct rhombohedron $r\{100\}$, and the complementary primary inverse rhombohedron $r'\{\bar{1}22\}$. These two latter rhombohedral forms apparently make up a doubly terminated hexagonal pyramid, but the two are often very unequally developed, and while the faces of the

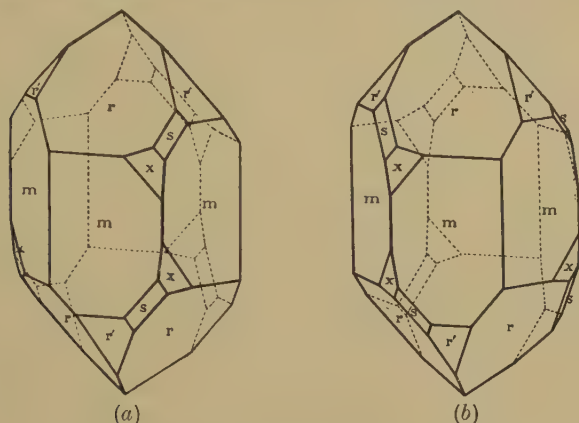


FIG. 57.—(a) Right- and (b) Left-handed Quartz Crystals.

direct rhombohedron r are usually brilliant and afford excellent signal images on the goniometer, those of the inverse rhombohedron r' are very frequently dull and badly reflecting. Now the two sets of s and x forms never occur together on the same crystal, unless the latter be a twin of the two varieties and not a single crystal; and consequently, if the crystal be a single one it is possible to recognise at once whether it is a right- or a left-handed one, by the position of these faces, whether they modify a right or left front solid angle, as shown in the two figures. The symmetry is thus clearly that of class 18, and the right and left general forms and the symmetry elements are shown in the next two figures, Figs. 58 and 59. The

elements of symmetry operating are (1) the indispensable trigonal axis, the vertical crystal-axis c , and (2) three digonal axes lying in the equatorial plane, identical with the three Bravais-Miller horizontal axes; there is, of course, no symmetry plane, this being one of the eleven enantiomorphous classes of crystals without symmetry planes.

Quartz is not a strongly doubly refractive substance, its two refractive indices being 1.5443 for sodium light for the ordinary ray ω , the vibrations of which occur perpendicular to the optic and trigonal axis c and in the circular section of the optical ellipsoid of revolution; and 1.5534 for the



FIG. 58.

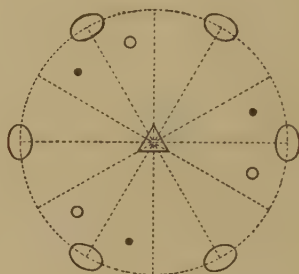


FIG. 59.

General Form and Symmetry Elements of Quartz Class.

extraordinary ray ϵ , with vibrations parallel to the axis, also for sodium light. The amount of double refraction for this radiation, $\epsilon - \omega$, is thus 0.0091, which is relatively small, that for calcite, of the trigonal class 21, being 0.1719. As ϵ is the larger for quartz, by convention the sign of the double refraction is positive. For calcite it is negative, the two indices of refraction ω and ϵ being 1.6583 and 1.4864 respectively, ω being thus the larger.

This can readily be illustrated by using a quartz prism of 60° refracting angle, the refracting edge of which is parallel to the crystal-trigonal and optic axis, to produce a spectrum instead of the ordinary glass prism in the spectro-scope, or for demonstration purposes in front of a project-

ing lantern provided with a slit and with the aid of a projecting lens. Instead of the usual single spectrum produced by a glass prism or train of prisms, we now see two spectra, in the spectroscope or on the screen, fairly close together and parallel to each other. If we then bring a Nicol prism, which only permits light vibrating in a single plane to pass, in the path of the rays, we observe that one of the two spectra extinguishes when the vibration plane of the Nicol is vertical, and the other when the Nicol is rotated so as to bring its vibration plane horizontal. The two spectra are, therefore, formed by rays which are composed of plane polarised light, and their planes are at right angles to each other. When the Nicol is at its 45° position, both spectra appear but with less intensity than when the Nicol is removed.

If we repeat the experiment with a prism of calcite instead of quartz, similar phenomena are observed, but the spectra are very much further removed from each other, indeed so far that both may not be got on to the same screen. Also one spectrum is much more dispersed (broader) than the other.

Now a thin section-plate of a uniaxial crystal, cut parallel to the axis, will show maximum double refraction effects in plane polarised light, when the vibration directions of the plate are in the neighbourhood of 45° to the planes of the two crossed Nicols. For the axis is the direction of single refraction, but double refraction begins as soon as we get away from it, and the further we recede the greater does the double refraction become. Hence, such a thin plate parallel to the axis in parallel polarised light, between crossed Nicols, while showing the dark field of crossed Nicols when its extinction positions parallel and perpendicular to the axis are parallel to the 0° and 90° planes of vibration of the Nicols, will at the 45° intermediate positions (that is, rotated 45° in its own plane from the 0° and 90° extinction positions), in most cases show brilliant colours,

in contradistinction to one cut perpendicular to the axis, which remains dark under crossed Nicols under all circumstances, however rotated in its own plane, just as would a plate of a cubic crystal or of glass, which are singly refractive (isotropic).

In the case of quartz, owing to its double refraction being only very moderate in amount, a section-plate of the usual thickness of rock-sections, about 0.04 mm., affords these colours in parallel polarised light most brilliantly, rendering quartz very easy to recognise under the polarising microscope. But calcite only gives white of the higher orders at this thickness, and a film of extreme tenuity is required in order to afford bright colours, owing to the unusually excessive amount of the double refraction. A rock section such as that of a granite, which contains free silica in the form of quartz, will illustrate this point well.

When we investigate the behaviour of thicker section-plates than those giving colour due to double refraction, at 45° to the extinction positions, we get very soon to paler and paler colours, and eventually to white of the higher orders and finally pure white light. So that such a plate, when rotated in its own plane, will merely appear four times dark and four times light, the dark maxima occurring at positions 90° apart, for which the planes of vibration of the crossed Nicols coincide with those of the crystal plate, and the light maxima occurring at the intermediate 45° positions. This occurs not only for plates parallel to the axis, but also for plates cut at some intermediate angle between this position and that perpendicular to the axis. If exactly perpendicular to the axis there is complete darkness for all positions, as already stated, however much it be rotated in its own plane.

But when we thus examine thicker and thicker plates of quartz, which are either intermediately cut or are actually perpendicular to the axis, we observe colour beginning to appear, and to be getting stronger as we pass

a thickness of two millimetres, until when we attain a thickness of between three and four millimetres the colours are quite brilliant, and at their maxima if the plate be cut truly perpendicular to the axis. If the plates had all been of quartz, and perpendicular to the axis in all cases, we should have observed the dark field becoming more and more invaded by coloured light. If the plate has truly parallel surfaces, and is from a single, totally untwinned, crystal, the colour will be even all over the field. Rotation of the analyser causes change of the colour, passing through the spectrum, the order (direction) being the opposite for the two varieties of quartz, right- or left-handed. When the section-plate is exactly 3.75 millimetres thick and the Nicols are parallel the colour exhibited is the so-called transition rose-violet. Further, the colour continues brilliant to beyond a thickness of 7.5 millimetres, and at this particular thickness the transition tint is produced when the Nicols are crossed, the reason for these two effects with parallel and crossed Nicols and plates of 3.75 and 7.5 millimetres being that under those respective circumstances the most brilliant part of the spectrum, the yellow (wavelength 0.000550 mm.) complementary to the transition rose-violet, is extinguished. More exact data for this will be given subsequently. Now all these colour effects with thick plates of quartz are due to optical activity.

Thus in the case of quartz two distinct and very brilliant sets of colour phenomena are observed in the dark field, and also some of them under parallel or intermediately placed Nicols, one due to double refraction, which makes its appearance only with very thin plates, and which exhibits itself at the maximum with plates parallel to the axis; and a second set due to rotation of the plane of polarisation of the light, which is only seen with thick plates, and is most intense when the plate is perpendicular to the axis.

It is an interesting historical fact that it was with quartz

that rotation of the plane of polarisation of light was discovered, by Arago, in the year 1811. It is supposed to be due to the two rays, which are propagated through the doubly refractive crystal, becoming circularly polarised, and to different amounts, owing to the screw-like structure of the crystal, and eventually by their mutual effects, one being retarded behind the other, becoming resolved on leaving the crystal into a plane vibration again, but rotated more or less from the original plane of vibration.

The relationship between the colour and the angle of rotation was investigated by Biot in the year 1813, who found that the amount of rotation is approximately inversely proportional to the square of the wave-length of the light. That is, the rotation has dispersion, the angle being different for the different parts of the spectrum. The amount of rotation is also directly proportional to the thickness of the plate, thus a plate 7.5 mm. thick gives twice the rotation of one of 3.75 mm. thickness, for light of the same wave-length. In order to measure the amount of rotation, therefore, pure monochromatic light must be used; and it is then found that the analysing Nicol requires to be rotated to a definite position for light of each wave-length in turn, in order to restore the dark field, this rotation of the Nicol corresponding to that of the optical rotation by the crystal.

Biot also established the rule for the order of appearance of the various colours of the spectrum as the analysing Nicol is rotated, when white light is being used, for the two varieties of quartz. He regarded as right-handed quartz that variety which, when the analysing Nicol is rotated clockwise, from left to right, when the observer is looking into the polariscope in the ordinary manner for a table instrument (be it either a table polariscope or a polarising microscope), affords the colours in the order of their refrangibility—the least refrangible red first, then orange, yellow, green, blue, and lastly the most refrangible violet; a left-

handed crystal he regarded as one which behaved in the converse manner on rotating the Nicol similarly clockwise, the colours succeeding one another being blue, green, yellow, orange, and red; or in the same manner (red, orange, yellow, green, blue) if the Nicol were rotated anticlockwise, from right to left.

It was not until later, in the year 1820, that Herschel discovered, and described to the Cambridge Philosophical Society, the little *x* and *s* faces indicative of right- and left-handedness on the crystals, and it is those crystals which have the little faces on the right which behave right-handedly according to Biot's convention, and those which have them on the left solid angles which are left-handed on the Biot convention. It is well to emphasise this, as much confusion has arisen in the past, largely owing to Herschel using the opposite convention to Biot, and imagining the observer swimming with the light, and to his giving a figure which he called that of a right-handed crystal, but which was really that of a left-handed one, and indeed a twin of two left-handed crystals.

In the case of the rotation of optically active liquids, which he also studied, Biot used his own convention consistently, cane-sugar in aqueous solution, for instance, being considered as right-handed, or dextro. According to Herschel, however, cane-sugar in solution rotates the plane of polarisation to the left, *lævo*. Biot's convention, needless to say, is the proper one to follow, for he initiated the subject and discovered the phenomena.

The amount of rotation of the plane of polarisation by crystals is conventionally expressed, in order to be strictly comparable, for a plate one millimetre thick and the temperature of 20° , as already mentioned. The specific wave-lengths of light, for which the observations are made, are of course given in each case, in order to render the observation exact and to indicate the dispersion of the rotation. For a quartz plate of either handedness the

following are the amounts of rotation for a graduated series of wave-lengths of the solar spectrum.

For solar line A	12° 39'
" " B	15 45
" " C	17 19
" " D	21 43
" " E	27 32
" " F	32 46
" " G	42 35
" " H	51 11

Many beautiful and highly instructive screen experiments can be performed with quartz section-plates cut perpendicular to the axis and of considerable size, preferably just large enough to be accommodated within the one and five-eighths inch circular aperture of the standard mahogany object carriers of the projection polariscope. When two large Nicol prisms, polariser and analyser, are available, together with separately mounted lens systems for projection in parallel and convergent light, all interchangeably mounted, with a suitable rotating object stage, on the same optical bench as the Nicols, and with a self-feeding and three-way adjustable electric arc in the lantern, the screen study of quartz can be very efficiently and delightfully carried out. A description of such an apparatus, used in the author's private laboratory, and of a typical series of experiments with quartz, will be found in Chapter L of the author's "Crystallography and Practical Crystal Measurement" (Macmillan, 2nd edition, 1922), and still others in Chapters XVI and XVII of his "Natural History of Crystals" (Kegan Paul, 1924).

The most instructive experiments in parallel light are those with both right- and left-handed plates of quartz of 3.75 and 7.5 mm. thickness, and with "biquartzes" of these thicknesses, consisting in each case of a right- and left-handed composite plate, the two oppositely rotating

halves being joined by balsam along a truly planed edge-face ground and polished at right angles to the plate, so as to appear as a mere line of demarcation on the screen, which practically disappears altogether when the two halves are arranged, by suitable rotation of the analysing Nicol, to show the same tint on the screen. The least rotation of the analyser from this position, however, causes the two halves to show marked difference in colour, the two colours being complementary, bright red and brilliant green for instance. Other biquartzes may instructively have the junction plane oblique to the plate, when a black band appears at the line of demarcation when the Nicols are crossed, and if the angle is as much as 45° it will show a coloured spectrum on each side of the black band, a white band separating it from each. Natural biquartzes, twins of right- and left-handed quartz with the junction plane perpendicular to the plate and parallel to the axis, are particularly interesting objects, and even more so from the spectacular viewpoint are others in which the junction plane is oblique, especially if also the twinning is repeated, say in one half of the composite plate only, while the other half is untwinned. Indeed sections in which the twinning is irregular and the interpenetration of one variety into the other erratic, afford the most surprising and gorgeous effects of colour on the screen. The culmination of beauty of quartz screen objects is, however, afforded by amethyst, the violet portions of this well known and highly prized variety of quartz consisting of regular closely laminated twinning of alternately right- and left-handed quartz, the individual laminae of which appear on the screen as regular closely ruled parallel lines of brilliant variegated colours, in which beautiful shades of grey often prevail, indicating the alternations of the two kinds, and those of each sector being arranged at 120° or 60° to those of the neighbouring sectors.

In convergent polarised light the plates of pure right- or

left-handed quartz of 3.75 and 7.5 mm. thickness show the uniaxial figure, but with the innermost circles of spectra somewhat squared, and without the central black cross, the black centre being now filled with the rotation colour of that thickness of quartz which would be given in parallel light. When the two 3.75 mm. plates (right and left-handed) are superposed, the famous Airy's spirals are afforded. These beautiful spiral figures are also given by the violet sectors of amethyst, owing to the fine and equal

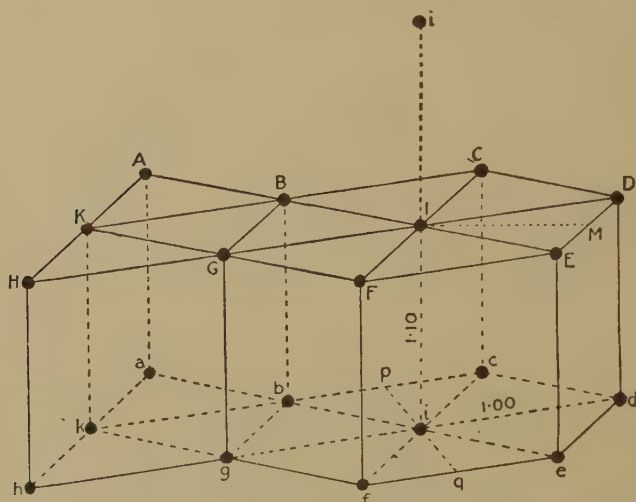


FIG. 60.—The Structure of Quartz (Space Lattice Cells).

blending of the rotation effects of the alternations of laminæ. Reference will be made later to these experiments with amethyst, as they afford an excellent gross illustration of the phenomenon of pseudo-racemism, a phenomenon to be dealt with in the next chapter.

Structure of Quartz.—The structure of quartz has proved difficult of elucidation by X-rays, but Sir William Bragg has eventually established that it is based on the hexagonal or trigonal 60° -prism space-lattice No. 6, as shown in Fig. 60.

The unit cell of the space-lattice contains three molecules

of SiO_2 , and there are three interpenetrating 60° -prism No. 6 lattices, one being derived from the other by a rotation of 60° about, and transition for $c/3$ along, the direction of the vertical trigonal axis. This axis therefore has the points arranged spirally around it, and the spiral may be right- or left-handed, corresponding to the two varieties of quartz. Fig. 61 shows this spiral arrangement of the atoms, the black discs representing silicon atoms and

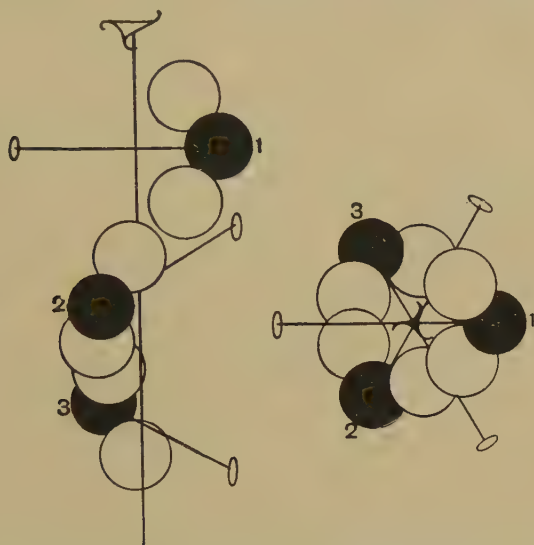


FIG. 61.—The Structure of Quartz (Spiral arrangement of Atoms).

the circles those of oxygen. There are three digonal axes intersecting in the vertical trigonal axis, a silicon atom lying on each. The axial ratio is $a : c = 1 : 1.100$, and the density is 2.65. The dimensions of the unit triangular prismatic cell are $a = 4.89 \text{ \AA.U.}$, and $c = 5.375 \text{ \AA.U.}$ The three molecules to the cell which these data indicate are arranged in such a way that planes of equal weight occur at $0, c/3, 2c/3, c$, etc., along the vertical axis c . The space-group or molecular arrangement is D_3^4 of Schoenflies or D_3^6 , the only difference between them being that one is right-

handed and the other left-handed, the X-rays being unable to distinguish one from the other.

The radius of the silicon spiral and the position of the oxygen atoms relative to the silicon atoms still remained to be determined, and R. E. Gibbs has since carried the subject further, working in Sir William Bragg's laboratory. He shows that the oxygen atoms do not lie in the same basal planes as the silicon atoms, but that there are successive silicon and oxygen planes perpendicular to the *c*-axis.

Their distance apart is 0.63 Å.U., one third of $c/3$, from determinations of the relative intensities of the various orders of X-ray spectra reflected from the basal plane of quartz. Now at 575° C. ordinary (α -) quartz becomes converted to β -quartz, and the intensities have been studied up to 800° C., as Backhurst had shown that the intensity of X-ray reflection slowly and regularly decreases on raising the temperature of the crystal. Gibbs finds marked intensity changes at the transition point, 575°. At this temperature the symmetry increases from trigonal to hexagonal, as proved by Laue photographs taken by Rinne, and by the etch-figures taken by Friedel, β -quartz probably belonging to the hexagonal trapezohedral class 24. The piezo-electric effect ceases at 575°, so this must be only a property of α -quartz; and the elasticity surface becomes one of revolution. The work of F. E. Wright on the changes of the rhombohedral angle of quartz has already been referred to on page 173. Rinne also remarked a change in refractive index, and Le Chatelier found a change in the coefficient of expansion law, an actual reversal of sign occurring at 575°, accompanied by a sudden expansion, both along and perpendicular to the axis. The specific heat also changes at 575°. Moreover, there is also a remarkable increase of electrical conductivity with temperature for the direction of the *c*-axis. Hence, all the physical properties studied show a gradual and continuous change up to 575°, when a discontinuous change to

a new state occurs, that of β -quartz, after which steady law again prevails. The new X-ray results confirm this. In cooling from above to below 575° , however, intricate internal twinning and optical changes occur.

If any two planes be chosen in α -quartz, making equal angles with the axis and meeting in a straight line perpendicular to the axis, they will in general differ in properties, but β -quartz should show no difference. Mandrot has tested this by cutting two sections parallel to the respective planes and determining Young's modulus with them, at temperatures both above and below the critical point. He found a large difference between the elasticities below 575° , but none above that point.

Sir William Bragg has kindly furnished the author with the data of further most interesting work in his laboratory, of which the following is a brief summary. A clear indication of gain of symmetry (to class 24) has been found on passing from α - to β -quartz, in the form of three new digonal axes of symmetry at right angles to the first and to the principal axis. The unit cell retains the same size and form, however, except for changes due to thermal expansion, and contains the same number of molecules. The oxygen atoms lie within the hexagon formed by joining the projections of silicon atoms, their distance from the edge being one-twelfth of the distance between two opposite sides of that hexagon (4.23 \AA.U.), that is, 0.35 \AA.U. It is then found that the oxygen projections form almost exactly squares of side 1.79 \AA.U. (0.33 would be exact). But this is also the value of $c/3$, the height of one oxygen plane above another. Hence the oxygen atoms lie at the four corners of a cube, the centre of which is a silicon atom. In other words, the oxygen atoms are arranged about the silicon atoms in the form of a regular tetrahedron, and the structure of quartz thus proves to be that of a pile of cubes. This is a remarkable and highly interesting result, when the tetravalency of silicon and its relationship to carbon are remembered.

All the various forms of twinning of quartz, even the more rare and obscure ones, are explained by this structure, and also both the pyro-electric and piezo-electric effects with quartz. There appears to be a separation of electricities between the silicons and the oxygens, the silicons being quadruply positive, and the oxygens doubly negative. On cooling half the triangles revolve through a small angle in one direction, and the other half in the opposite direction, the balance being thereby destroyed so that charges are developed at the ends of the digonal axes (which are also the electric axes). Pressure along an axis does not merely cause rotation of the triangles, as for the pyro-electric effect, because the result would be electrification along all three axes alike, which is not the case. The electrification due to pressure must involve an actual distortion of the triangle. Thus are all the wonderful properties of this most interesting of minerals shown to be functions of its intricate crystal structure.

CHAPTER X

ENANTIOMORPHISM AND OPTICAL ACTIVITY. TARTARIC ACID AS EXAMPLE

THE experience gained from the study of quartz will have paved the way for the clear understanding of the connection between enantiomorphism of crystal form, optical rotation, and chemical constitution, as well as of the nature of the phenomena of optical activity. The discovery of the connection as regards chemical constitution we owe undoubtedly to Pasteur, whose very first research yielded this rich result. In the year 1769 Scheele isolated the now well-known organic acid, tartaric acid, as the result also of his first research. In 1819 another organic acid greatly resembling tartaric was found in the grape-juice vats at Thann in Alsace, and it was investigated by Gay-Lussac in 1826 and by Gmelin in 1829, in both cases with no satisfactory result. Gmelin called it "Traubensäure"—acid of grapes, which in France and England was Latinised into "Racemic acid," from *racemus*, a bunch of grapes. Berzelius afterwards tackled it with more success, and proved definitely that its empirical composition is the same as that of tartaric acid, $C_4H_6O_6$. This observation, moreover, became famous as the first case of a new phenomenon or principle in chemistry, that now so well known as "Isomerism."

Subsequently Biot, in the course of his pioneer work on the rotation of the plane of polarisation of light, examined both tartaric and racemic acid for optical activity. He found that the solution of the crystals of tartaric acid in water rotated the plane of polarisation to the right, but that racemic acid is optically inactive.

In the year 1848 Pasteur took up the subject, studying first racemic acid and its salts. Among other observations he found that if ammonium hydrate be added to an aqueous solution of the most readily preparable salt, sodium hydrogen racemate, and the solution be set to crystallise, the salt sodium ammonium racemate, $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, separates in crystals which gave him the key to the mystery. For he observed that in some of the crops all the crystals were either right-handed or left-handed, the two varieties when equally developed being the mirror-images of each other. Further, crystals of either kind could be got at will, by touching a metastable solution (one saturated at 28°C . and cooled to the ordinary temperature serves best) with a crystal of the desired variety. These crystals belonged to the rhombic bisphenoidal class 6, one of the eleven enantiomorphous classes possessing no plane of symmetry, the faces of complementary bisphenoids being present on opposite sides of the two kinds of crystals. On redissolving each kind separately and recrystallising, that same variety again crystallised out. Next, on precipitating a solution of each variety separately with a soluble lead salt, and decomposing the precipitate with sulphuretted hydrogen, Scheele's ordinary (dextro) tartaric acid was obtained in one case, while in the other a new form of tartaric acid was obtained, the aqueous solution of the crystals of which rotated the plane of polarisation to the left. Lastly, on mixing solutions of the two separate acids thus obtained, dextro and lævo, heat was evolved and a molecular combination of the two was formed, which crystallised out with a molecule of water of crystallisation, and was racemic acid, $\text{C}_4\text{H}_6\text{O}_6 \cdot \text{H}_2\text{O}$. The difference between ordinary tartaric acid and racemic acid, therefore, is that the ordinary is dextro-tartaric acid, while racemic acid is a molecular compound of equivalent quantities of dextro- and lævo-tartaric acids, the two equally and

oppositely rotatory varieties neutralising one another in the combination.

It was found later (1865) by Scacchi that the more strictly accurate explanation of what had occurred is as follows. Sodium ammonium racemate is a crystalline (monoclinic holohedral) salt of the composition $C_4H_4O_6(NH_4)Na \cdot H_2O$, which, when recrystallised at temperatures below 27° is deposited as a mixture of right- and left-handed crystals of the two optically active tartrates $C_4H_4O_6(NH_4)Na \cdot 4H_2O$. Above 27° the racemate is the stable crystal form, but below this transition temperature the equimolecular mixture of the two tartrates is the stable solid phase in equilibrium with the inactive solution.

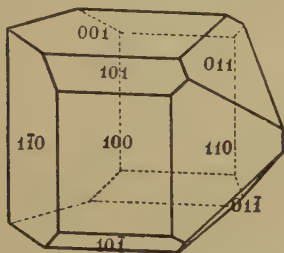


FIG. 62.—Dextro-tartaric Acid.

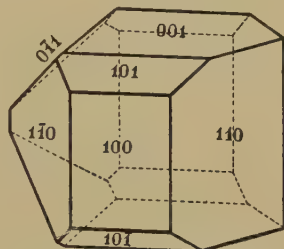


FIG. 63.—Lævo-tartaric Acid.

If equal proportions of the two tartrates are mixed at 27.2° they are transformed to the racemate, and $3H_2O$ are set free. But an actual racemic compound does not exist in solution.

Pasteur measured some good crystals of ordinary dextro-tartaric acid, and carried out sufficient observations with the lævo-acid to satisfy himself that its crystals are mirror-images of the dextro-rotatory crystals. They belong to the monoclinic sphenoidal class 4, another of the eleven enantiomorphous classes. Two typical specimens are shown in the two figures above.

These crystals are clearly mirror-images of each other. Owing to the absence of the symmetry plane possessed by the holohedral class 5 monoclinic crystals the two varieties

are complementarily hemimorphic as regards the faces at the two ends of the lateral symmetry axis b , the four-faced clinoprism $\{011\}$ of class 5 being divided into two two-faced forms, the right clinoprism $\{011\}$ and the left clinoprism $\{0\bar{1}1\}$, the former being characteristic of dextro-tartaric acid and the latter of lævo-tartaric acid.

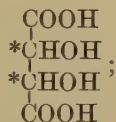
The crystals of the two optically active varieties of tartaric acid are anhydrous $C_4H_6O_6$, whereas racemic acid, as just indicated, crystallises with a molecule of water of crystallisation (although Scacchi later got an anhydrous racemic acid, also triclinic but differently), and in another system of symmetry, namely, in the pinakoidal holohedral class 2 of the triclinic system. It is also a single substance, of one form only, class 2 not being one of the eleven enantiomorphous classes. It is, however, only a somewhat loose compound, as molecular compounds often are, and is divisible into its two components, the right and left varieties of tartaric acid, under the specific circumstances which have been stated.

Two years afterwards, in 1850, Pasteur discovered a fourth kind of tartaric acid, now known as meso-tartaric acid, which is truly and unresolvably optically inactive, and in explanation he discovered the generalisation which has since become known as "Pasteur's Law." This important principle, which shows that the whole matter is a question of molecular symmetry or the lack of it, was enunciated essentially as follows. "If the atoms of a chemical molecule be dissymmetrically arranged, the existence of two oppositely complementary configurations of the molecule is possible, both varieties having the same chemical properties and equal but oppositely directed rotatory power. The presence of molecular dissymmetry therefore reveals itself by this rotatory power of the molecules, and is wholly determined by their chemical constitution. When the atoms of a chemical molecule are dissymmetrically arranged, the fact is at the same

time betrayed by the occurrence of the two varieties in complementary non-superposable crystalline forms possessing screw axes of opposite winding."

As regards the two enantiomorphous varieties, we are obviously in the presence of physical isomerism, as distinguished from chemical isomerism. But as regards racemic acid, it is chemical isomerism; for this is a distinct chemical compound, the molecular compound of the two physical isomers, and the crystals are entirely different, the system of symmetry being different.

The optical activity of carbon compounds has since been identified by Van 't Hoff and Le Bel as being connected with the possession of a so-called "asymmetric" carbon atom, one the four valency bonds of which are satisfied by four quite different elements or radicle groups. Tartaric acid possesses two such carbon atoms, those of the two CHOH groups, starred in the accompanying constitutional formula,



each of these two carbon atoms is attached by one bond to a hydrogen atom, by another to the oxygen atom of a hydroxyl OH group, by a third bond to the carbon atom of a COOH group, and by the fourth to the other asymmetric carbon atom. Hence, the group of atoms in one half molecule may be arranged either symmetrically or unsymmetrically with respect to those of the other half molecule. If they are symmetrically arranged the whole molecule will be inactive, and this is the condition in meso-tartaric acid. That is, the molecule of meso-tartaric acid has a plane of symmetry. If they are unsymmetrically arranged, they may be so in a right-handed or left-handed manner, the two arrangements being as the mirror-images of each other; this is the case of the two optically active

varieties, dextro- and lævo-tartaric acids, their solutions being active also as the molecules themselves are enantiomorphous. Racemic acid is the more or less loose molecular compound of the two, the case of external compensation, whereas meso-tartaric acid is the case of internal compensation.

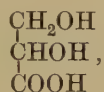
Quite recently, however, F. M. Jaeger has shown that, although practically all known optically active carbon compounds do possess asymmetric carbon atoms, there would appear to be a few exceptions, and that the only absolutely sound criterion is the absence of second order symmetry elements, planes of symmetry and second order axes, and the presence of only first order, axial, symmetry elements. That is, if the stereometric configuration of the atoms in the molecule possess only first order axial symmetry, the substance is resolvable into two enantiomorphous components, which are the optical antipodes of each other; but if a second order symmetry element, especially a symmetry plane, be present, the compound will not be capable of such resolution, even although several asymmetric carbon atoms be present. This is the case with meso-tartaric acid, which is inactive because it has a plane of symmetry, although it has two asymmetric carbon atoms.

Pasteur somewhat later made the further remarkable observation that when the spores of the ferment *Penicillium glaucum* are added to a solution of racemic acid containing a small quantity of phosphates, which would appear to be essential to the life of the organism, the dextro component of the molecular compound is devoured by the organism, while the lævo component is unacted upon so long as any dextro remains. Why this selection occurs is one of the mysteries of life, but the fact is a fortunate one for enabling the lævo variety to be isolated, and it was thus obtained practically pure by Pasteur.

These remarkable researches on tartaric acid have

proved to be pioneers, for very similar results have been since obtained with regard to a very considerable number of carbon compounds. For the molecular combination of two enantiomorphous varieties of an optically active carbon compound has been found to be a general principle, so much so that it has come to be called "racemism," and the compound a "racemic" one. Moreover, the use of ferment-organisms has become likewise a general process for the separation of the two optical antipodes; for it has again proved fairly general that the organism eats up one kind and leaves the other, as if it could only assimilate one of the two kinds of helix of atoms. The crystal structure of the racemic compound is always different, being that of a different chemical substance, from that of the two enantiomorphs; but some morphotropic (isogonal) resemblances are sometimes observed.

An instance which has come under the author's own experience is that of glyceric acid, the calcium salt of the dextro variety of which was investigated by the author in the year 1891. Glyceric acid,



has one asymmetric carbon atom, that of the central CHOH group. It is itself viscous and uncrystallisable, but its calcium salt, $\text{Ca}(\text{C}_3\text{H}_5\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, crystallises well. When its solution is fermented by the *Bacillus ethaceticus* one half of the glyceric acid is eaten out, the lævo half, and the remainder, after precipitation of the calcium by oxalic acid, is dextro-rotatory. When the calcium salt of this dextro-rotatory variety is prepared, the crystals are found to be enantiomorphous, belonging to the same monoclinic sphenoidal class 4 as tartaric acid, and showing certain forms only on the right and others only on the left. Its solution is lævo-rotatory. All the goniometrical and

optical constants were worked out, and the similarity to the case of tartaric acid clearly established.

It should be made perfectly clear that ordinary tartaric acid is known as the dextro-rotatory variety because its solution in water rotates the plane of polarisation to the right, on the accepted convention of Biot (p. 189); indeed Biot himself first showed this (p. 197). The crystals of ordinary tartaric acid, however, were only studied first adequately as regards their optical activity by Dufet,* in 1904, the determination being a very difficult one for a monoclinic crystal, requiring section-plates perpendicular to each of the two optic axes. He found that for a plate in each case one millimetre thick the rotation (which was equal for the two optic axes, their plane being perpendicular to the possible symmetry plane of the monoclinic crystals, $b\{010\}$) was: for red lithium light -8.5° , for yellow sodium light -11.4° , and for green thallium light -14.2° . The specific rotation of aqueous solution of tartaric acid is $[\alpha]_D^{20} = +15.06$. For the sake of comparison it may be mentioned that the specific rotation of aqueous solution of cane sugar is $[\alpha]_D^{20} = +66.7^\circ$. A millimetre layer of the solution of tartaric acid and of cane sugar respectively, corresponding to the plate of crystal one millimetre thick, would only rotate the plane of polarisation of sodium light for 0.151° and 0.667° , the crystals being much the more powerfully rotatory.

Pasteur was born on December 27th, 1822, and in December 1922 a paper was presented to the Royal Society by Mr. W. T. Astbury describing the successful X-ray analysis of tartaric acid, carried out in Sir William Bragg's laboratory, fully confirming the work of Pasteur and affording a remarkable insight into the crystal structure of the two varieties. Two asymmetric molecules $C_4H_6O_6$ were found to be contained in the unit cell of the space-lattice. The expected spiral structure was revealed, and

* *Bull. Soc. fr. min.*, 1904, 27, 163.

in fact two spirals are present of different winding, but not mirror-images of each other. One is in the interior of the molecule itself, being associated with the four carbon atoms of the centre of the molecule, which are situated at alternate corners of the oblique parallelepiped; it therefore remains permanent when the crystal is dissolved in water, and causes the dextro-gyratory optical activity of the solution of ordinary tartaric acid. The other is a twist caused by the necessity of fitting the molecules in their places, and is associated with the four hydroxyl groups;

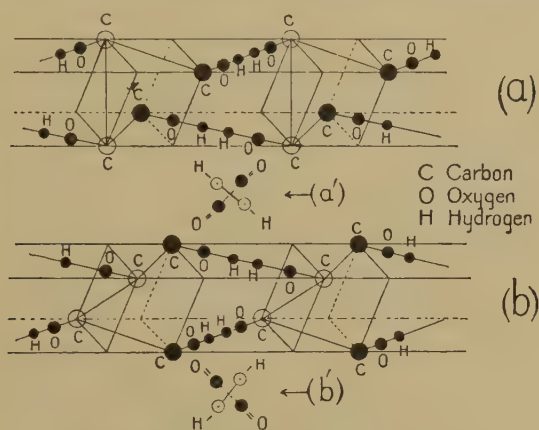


FIG. 64.—The Structure of Tartaric Acid.

it is thus a peculiarity of the crystal structure only. Being of inverse sign to the other, lævo-gyratory in the case of ordinary tartaric acid, and more powerful in its effect on light, it imposes, in the net result of the two rotations, its sign on the rotation of the plane of polarisation by the crystals. The two molecules in the cell are of the same variety, definitely either right (in ordinary tartaric acid) or left (in the lævo acid), and not of the two different varieties, so that there is no internal compensation. The three accompanying figures illustrate the results.

The first, Fig. 64, shows the two structures, right (ordinary tartaric acid) and left (the lævo acid), at (a)

and (*b*) respectively, two molecules end to end in each case, with cross sections *a'* and *b'*. The second, Fig. 65, shows the arrangement of the molecules in the cell, each molecule being represented by a diagrammatic "shoe," all the "shoes" being of one kind only, to indicate the asymmetry, for each molecule in tartaric acid is definitely

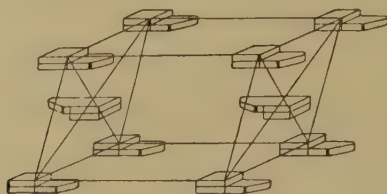


FIG. 65.—Arrangement of Molecules in Tartaric Acid.

proved to be asymmetric. The third, Fig. 66, represents the arrangement of the atoms in one molecule or "shoe." This structure agrees perfectly with the fact that the plane of the optic axes is perpendicular to the one possible symmetry plane of the monoclinic crystal, which is a principal plane of the optical ellipsoid, and with the con-

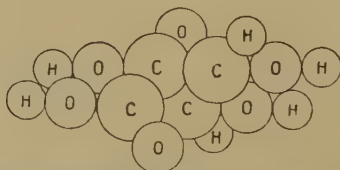


FIG. 66.—Arrangement of Atoms in Molecule of Tartaric Acid.

sequential fact that the optical rotation exhibited by the crystal along the directions of the two optic axes, where alone optical activity can be studied (with two plates, one perpendicular to each optic axis) relatively free from double refraction effects, is the same. As already mentioned, Dufet found it to be $-8^{\circ} 33'$ for red lithium light per millimetre of thickness of crystal plate, $-11^{\circ} 24'$ for yellow sodium light, and $-14^{\circ} 14'$ for green thallium light.

Thus the final conclusion is that the dextro-rotatory

power of ordinary tartaric acid in aqueous solution is due to a spiral arrangement of the atoms in the molecule, and the lævo-rotatory power of the crystals to a second more powerful and oppositely wound spiral in the crystal structure, which more than neutralises the dextro-gyratory effect of the molecules themselves. Also that in the lævo variety of tartaric acid the conditions are the converse.

Mr. Astbury has since investigated racemic acid (the anhydrous acid of Scacchi) by X-rays, and finds, as might have been expected, that two molecules of tartaric acid

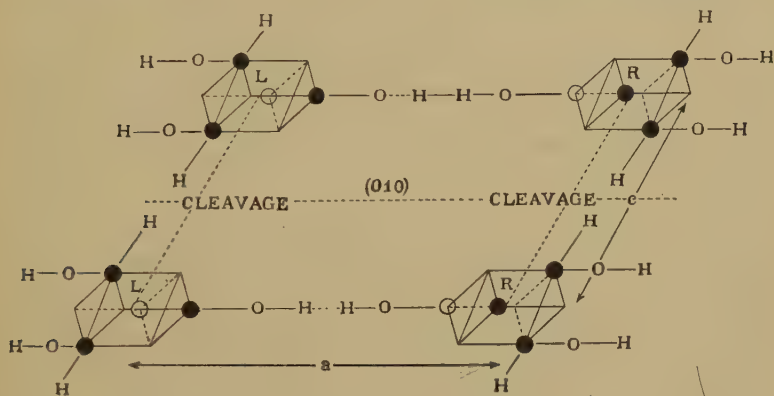


FIG. 67.—Structure of Racemic Acid.

$C_4H_6O_6$ are contained in the unit cell of the triclinic space-lattice, but that the two are the mirror-images of and centro-symmetrical to each other, one being right-handed and the other left-handed. This corresponds perfectly to external compensation in a molecular compound of the two varieties. The structure is shown in Fig. 67, and it explains fully all the known properties of racemic acid. The black spots represent the four carbon atoms of the asymmetric molecule, arranged tetrahedrally at the four alternate corners of the monoclinic parallelepiped of an active tartaric acid molecule, right- or left-handedly. The absolute dimensions of the cell indicate a molecular contraction on mixing dextro- and lævo-tartaric acids to form

racemic acid, and this explains the observed evolution of heat during the mixing. It is most satisfactory that this further appeal to X-rays should so completely substantiate the work of Pasteur.

Pseudo-Racemism.—There is yet another type of organic compound which is optically inactive owing to external compensation, but without being a molecular compound like racemic acid. It is due to the repeated and very closely intercalated twinning of the two optical antipodes. It is easy to imagine repeated lamellar or other intimate kind of twinning becoming so fine as to approach molecular dimensions, that is, that the individuals are only a few molecules thick, and to be so regularly and equally intercalated that in the whole crystal the optical activity of the two varieties is exactly neutralised. Such a crystal simulates usually the symmetry of the holohedral class of the system, the sum of the two symmetries of the right and left enantiomorphs. It is not a new chemical compound like a racemic one, showing entirely different symmetry, but the same chemical compound displaying the symmetry of its two varieties in summation. To such a substance the term "Pseudo-racemic" has been applied. It is very well, but grossly, illustrated by the twinned intercalation of the two varieties of quartz in amethyst. We have only to imagine the repeated twinning in the fine lamellæ, which have been described as characteristic of the purple sectors of an amethyst, to become finer and finer until they first become submicroscopic and then eventually so extremely fine as to be only a few molecules thick. No microscope or polariscope would then reveal them, and just as even amethyst, with its relatively coarse twin-lamellæ, affords Airy's spirals in convergent polarised light, the characteristic figure of the intimately twinned two varieties of quartz, so all the more perfectly will a pseudo-racemic crystal exhibit the combined characteristics of the two intercalated enantiomorphous varieties,

which together make up the holohedral form, or at any rate a higher class, of the system of symmetry developed.

One of the substances which have been described as pseudo-racemic by Sir William Pope and Prof. Kipping, who have described quite a number of examples, is *sobrerol*, $C_{10}H_{18}O_2$, an organic compound first studied in 1892 by Miers (now Sir Henry) and Pope. It crystallises in the same monoclinic spenoidal class 4 as tartaric acid, and forms two active varieties, *dextro* and *lævo*, which when their alcoholic solutions are mixed in correct equimolecular proportions unite (physically only) to deposit crystals showing the combined symmetry of the two. It is not such a clear case, however, as those of some later but much more complicated compounds, for the symmetry is at the same time enhanced to rhombic. The axial ratios, however, are almost identical with those of the two enantiomorphs, and the density is exactly the same. The substance is quite inactive optically, and was proved by Miers and Pope to be a mechanical mixture of the two enantiomorphs, which are so equally present as to neutralise each other's opposite rotatory effects. On heating these crystals of *sobrerol*, they become converted into a truly racemic inactive form, the mixture, already approaching one of molecular dimensions, having now actually become truly molecular; and having thus passed within the range of molecular forces and those of the milder chemical nature which give rise to molecular combination, a molecular, racemic, compound has been produced. Some extra heat is required to undo this racemic compound, so that the melting point of inactive *sobrerol* is higher than that of the two enantiomorphous optical antipodes.

Generally, however, the pseudo-racemic form of a substance which usually crystallises in two optical antipodes merely shows the combined symmetry of the two, that is as a rule, the holohedral symmetry of the system to which the two enantiomorphous varieties belong, without any

enhancement of system ; but occasionally, as with *sobrerol*, enhancement of system does also occur. The definition of Pope and Kipping may be taken as the best yet given of the phenomenon of pseudo-racemism, and it is as follows :—

“A pseudo-racemic substance is an intercalation of an equal proportion of two enantiomorphously related components, each of which preserves its characteristic type of crystalline structure, but is so intercalated with the other as to form a crystalline individual of non-homogeneous structure. A solid racemic compound, on the other hand, is a crystalline substance of homogeneous structure which contains an equal proportion of two enantiomorphously related isomerides. An inactive externally compensated substance, which closely resembles its active isomerides crystallographically, is to be considered as pseudo-racemic, whereas when the contrary is true it is to be regarded as racemic.”

CHAPTER XI

REMARKABLE CASES AND GENERAL CONCLUSIONS CONCERNING OPTICAL ACTIVITY

IT has been already mentioned that more recent researches, and experience with the many optically active substances which have been discovered since the time of Pasteur, have made it clear that the really essential condition for the display of the property of the rotation of the plane of polarisation of light is the absence of second order symmetry elements. It would appear, indeed, that besides the absence of a plane of symmetry and of a centre of symmetry there must also be the absence of an axis of the second order. Axes of the second order are such that a rotation around them for their characteristic angle is always inseparably accompanied by, and combined with, a reflection of the figure in its new position in the imaginary mirror, the plane of which is imagined to be at right angles to the axis, its normal. By the movement around such an axis, and the reflection, the figure is always transformed into its image, or is inverted. The only symmetry elements which are operative when a figure differs from its image are simple axes of rotation, such as all the eleven enantiomorphous classes of crystals possess, without any other symmetry element.

The condition formerly considered as the indispensable one, the presence of one or more asymmetric carbon atoms, has been found to fail in a few recent cases. That of inosite, $C_6H_6(OH)_6$, for instance, the molecule of which possesses only axial symmetry and yet has no asymmetric carbon atom, is a good example. The dextro and lævo

varieties of this substance have been isolated by Macquenne and Tanrét. Similar cases, but very complicated organic compounds, have also been described by Pope and Perkin, and by Mills and Bain.

Jaeger mentions two cases of organic compounds possessing several asymmetric carbon atoms, and neither a plane nor a centre of symmetry; yet, because they possess second order axes they are identical with their own images, and are not resolvable into optical antipodes. The first is a derivative of tetramethylmethane, and possesses four asymmetric carbon atoms, but a second order tetragonal axis. The second is a derivative of tetramethylene, and although possessing no less than eight asymmetric carbon atoms, is unresolvable, as it also possesses a tetragonal axis of the second order.

Most of these considerations, however, apply to the chemical molecules, and their optical activity in the liquid or dissolved state. As so many of these organic compounds crystallise in the systems of low symmetry, especially the monoclinic, the investigation of the crystals for optical activity is a matter of some difficulty. For there is no direction of absolute single refraction, as along the optic axis of a uniaxial (trigonal, tetragonal, or hexagonal) crystal, and the apparently analogous pair of optic axes of a biaxial (rhombic, monoclinic, or triclinic) crystal are not directions of absolutely single refraction. Moreover, instead of the whole dark field of the polariscope being available, for examination for the expected uniform display of colour, as with a section-plate perpendicular to the axis of a uniaxial crystal, there is only the dark centre of the field, the vertex of the hyperbolic "brush," really available, when one is studying a plate perpendicular to one of the two optic axes of a biaxial crystal. And further, both optic axial directions have to be studied, for the amount and even the sign of the rotation differs in the two cases, unless the optic axial plane happens to be

perpendicular to a possible symmetry plane of the system of symmetry developed, as it always is with a rhombic crystal but is only occasionally so with a monoclinic, the most frequently recurring system, which has only one possible symmetry plane. Also the positions of the optic axes have to be sought for, and when found section plates have to be ground or cut out of them, a matter of great difficulty unless one possesses a cutting and grinding goniometer such as that of the author. Hence it is that so few determinations of the optical rotation of crystals have been carried out up to the present. For if the section-plates are not truly orientated double refraction and other optical phenomena are so much in evidence that the presence of optical activity is not readily detected. Also the optical activity itself diminishes very rapidly as the true direction of the optic axis is departed from.

With these facts borne in mind, however, the presence of an asymmetric carbon atom in a new compound might properly suggest an investigation for optical activity, as the vast majority of optically active compounds do possess one or two such atoms. Moreover, Kipping has shown that an asymmetric pentavalent nitrogen atom also gives rise to optical activity in two optical antipodes. Sir William Pope, as well as Kipping and others, have also shown that in certain compounds an asymmetric tetravalent atom of either sulphur or its family analogue selenium, or even an asymmetric atom of tetravalent tin, may cause optical activity in two enantiomorphous varieties. Lastly, Meisenheimer and Lichtenberg, and also Kipping, have described enantiomorphous optically active substances containing an asymmetric pentavalent atom of phosphorus. So that the phenomenon is by no means confined to the compounds of carbon and (as Kipping showed) its analogue silicon.

With regard, however, to the best manner of regarding this question of an asymmetric polyvalent atom causing

optical activity, a statement in the presidential address of Sir William Pope to the Chemical Section of the British Association in 1914 may be quoted. "It must be insisted that the observed molecular activity is the result of the enantiomorphism of the molecular configuration; the asymmetry of a particular atom is not to be regarded as the cause of the optical activity, but merely as a convenient geometrical sign of molecular enantiomorphism."

Remarkable Cases of Optical Activity.—Some cases of optical activity of a new type, and distinguished by remarkably large amounts of rotation of the plane of polarisation, have recently been described by Werner, and followed up with great success by F. M. Jaeger. In his researches on the complex compounds of trivalent metals Werner found that some of them could be separated into two oppositely optically active varieties. They are of the type $[M \cdot X_3]R_3$, where M is a trivalent metal such as cobalt, chromium, rhodium, or iridium, X is a dibasic acid radicle such as that of oxalic acid, or a divalent pseudo-base, such as ethylene diamine $C_2H_4(NH_2)_2$, and R is a halogen or an acid radicle such as that of nitric or sulphuric acid, or even, which appears curious, the metal potassium. For Werner found that in the complicated ammonium compounds of chromium, cobalt, rhodium, and iridium, he could replace the six ammonium radicles by the three radicles above mentioned. It then happened that the three identical radicles grouped themselves around the trivalent metallic atom in such a manner that the molecule is not identical with its own image, and formed two varieties which were each other's mirror-images. There is no question of asymmetry of the central metallic atom, but only the configuration of the molecule in question, no second order symmetry element being present. Both the solutions and the crystals show very large amounts of optical activity.

The most remarkable of these salts, which has been very

fully investigated by Jaeger, is cobalti-trioxalate of potassium, $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3$, which crystallises in the triclinic system with three and a half molecules of water of crystallisation (that is, two molecules of the compound crystallise with $7\text{H}_2\text{O}$), as a racemic salt, at a temperature only just above the freezing point of water and in the dark. At ordinary summer temperature, about 18°C ., in a dark room, however, quite different dark green trigonal crystals separate with one molecule of water, $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot \text{H}_2\text{O}$, which are found to be a mixture of the right- and left-

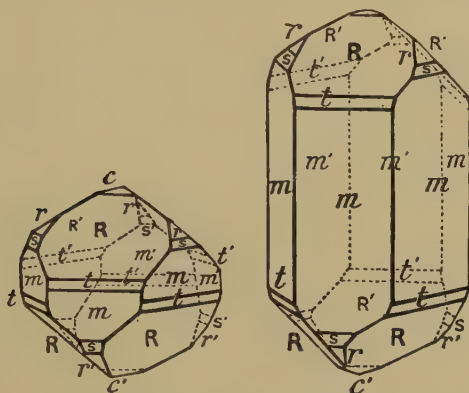


FIG. 68.

FIG. 69.

Dextro and Laevo Crystals of Potassium Cobalti-Trioxalate.

handed optical antipodes. A very distinct temperature of transition from the racemic triclinic form to the enantiomorphous trigonal form was observed, namely, 13.2°C .

Two typical crystals are shown above. They belong to the quartz class 18. The enantiomorphous class-determining form $x\{22\bar{4}1\}$ is not shown, as its faces were very minute; but they were quite clearly observed and their positions determined. The molecular rotation $[\text{M}]_{\text{D}}^{20}$ in solution is given by Jaeger as no less than $11,000^\circ$, and this is comparable to 280° for cane-sugar under like circumstances. The specific optical rotatory power corresponding to it is $[\alpha]_{\text{D}}^{20} = 2,407^\circ$, whereas $[\alpha]_{\text{D}}^{20}$ for sugar is usually

given as 66.7° , on the assumption that $[\alpha]_D^{20} = \frac{\alpha}{l \cdot d}$ and that the molecular optical rotatory power is $[M]_D^{20} = \frac{m}{100} \cdot \frac{\alpha}{l \cdot d}$, where m is the molecular weight, l the length of the solution (in the tube of the polarimeter), and d its density. These comparative data for this remarkable substance potassium cobalti-trioxalate and cane-sugar will enable some idea of the very large rotation of the former to be obtained, forty times that of the latter.

Three other salts of the composition $\left[\text{Co} \begin{smallmatrix} (\text{C}_2\text{O}_4) \\ (\text{Eine})_2 \end{smallmatrix} \right] \text{Br}$, where Eine represents ethylene diamine, $\left[\text{Cr} \begin{smallmatrix} (\text{C}_2\text{O}_4) \\ (\text{Eine})_2 \end{smallmatrix} \right] \text{Br}$, and $[\text{Co}(\text{Eine})_3]\text{I}_3$, afforded respectively molecular rotations of 2525° , 1100° , and 1072° .

It may now be well to summarise the broad facts as to the connection between crystalline form and optical activity.

Summary regarding Optical Rotation.—(1) All optically active substances which are solids at ordinary temperature crystallise in one of the eleven enantiomorphous classes possessing no plane of symmetry. It may not be easy to recognise the enantiomorphism, as only the primary faces common to the holohedral and the enantiomorphous classes of the system may be developed, and none of the faces special to the lower class.

(2) All substances crystallising in one of the eleven enantiomorphous classes of symmetry are not optically active, as some do not possess screw axes. This is the case with barium nitrate.

(3) In the cases of optically active liquid substances, it is the molecules themselves that are enantiomorphous, that is, are dissymmetric.

(4) Three classes of substances, including the liquids or solutions referred to under (3), and which may be considered as class (a), are to be distinguished as possessing

the power of rotating the plane of polarisation of light. The other two are : (b) Those which are solid and form crystals which exhibit two enantiomorphous varieties belonging to one of the eleven classes of symmetry without symmetry planes, and which are optically active, but the solutions of which are optically inactive; in these cases the optical activity is entirely due to the helical crystal structure. Sodium chlorate, NaClO_3 , is a capital instance, only the crystals being optically active, and the solution inactive. (c) Those which exhibit rotatory power both in solution and the crystalline state. In this last mentioned case (c), the rotation may be of opposite sign in the crystals to what it is in the solution, as in the case of tartaric acid. The molecules themselves as well as the crystal structure are in these cases both unsymmetrical.

(5) Chemical molecules in which the atoms are arranged with only simple rotation-axial symmetry, and with no symmetry plane or other symmetry element of the second order, afford the possibility of separation into two enantiomorphously related varieties, physical isomerides, having opposite rotatory power.

(6) If a chemical compound possess an asymmetric atom of an element of valency greater than triadic, the compound may generally be resolvable into two enantiomorphously related physical isomerides of opposite optical rotatory power.

(7) The possibility of fission into two such physical isomers is not restricted to the cases (coming under (6)) with an asymmetric plurivalent atom, but is essentially dependent on having a stereometric configuration endowed with only axial symmetry (as stated under (5)). Indeed no asymmetric atom need be present, and even if several such atoms are present it may occasionally happen that the compound is optically inactive.

(8) A racemic compound is a molecular compound of the two, dextro and lævo, enantiomorphous physical isomers, and usually crystallises quite differently from the latter.

It is generally separable into its two components, either by crystallisation under specific conditions, inoculation with a crystal of one of the component isomers, or by means of a ferment organism. Racemic compounds appear only to exist in the crystalline condition, and not in solution, which generally dissociates them into their two enantiomorphous components.

(9) A pseudo-racemic compound is an intimate mixture, twinning, or intercalation of the two unchanged enantiomorphous varieties, and shows either the combined symmetry of these two forms, that is, enhancement of class usually to the holohedral class of the same system, or occasionally with symmetry enhanced to the next higher system, but with close isogonality with the two enantiomorphs.

(10) A truly inactive form of the compound may exist if the molecule can possess a plane of symmetry, by the more symmetrical arrangement of its atoms than occurs in the enantiomorphous forms. Thus in tartaric acid the two halves of the molecule, which possesses two asymmetric carbon atoms, are differently arranged with respect to each other in the enantiomorphs, dextro- and lævo-tartaric acids, the whole molecule being asymmetric; but they are arranged symmetrically with respect to each other, mirror-images, with a plane of symmetry, that of the imaginary mirror, between them, in truly inactive tartaric acid, known as meso-tartaric acid.

In concluding this portion of the subject it is not too much to say that the work of Pasteur on tartaric acid, which has been so fully substantiated by the critical analysis by means of X-rays in these later days, has proved to be the basis of the great subject of Biochemistry, which has grown of late to such dimensions that we now have, in Cambridge and Oxford, great departments of study devoted to the subject, and the example set by which is being rapidly followed by universities all over the world.

CHAPTER XII

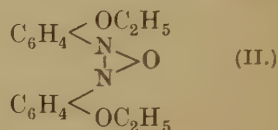
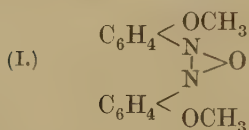
“ LIQUID CRYSTALS ”

It is curious what accidents lead to entirely new fields of research and to discoveries of importance. Prof. Otto Lehmann, of the Technische Hochschule at Carlsruhe, was working, in the year 1876, with a remarkable substance, silver iodide, AgI , which crystallises at ordinary temperatures in the hexagonal system, but which Mallard and Le Chatelier had shown to be dimorphous, becoming converted at 146°C . into a cubic modification with absorption of heat. Long before this, in 1867, Fizeau had shown by direct measurement with his interference dilatometer (referred to on p. 60 in Chapter III) that silver iodide is one of the few exceptional substances that contracts on heating, a feeble expansion in directions perpendicular to the hexagonal axis being greatly overbalanced by a considerable contraction along the axis.

Now Lehmann was studying the cubic modification which is the culmination of the contraction, and thought that he found it to be so plastic as to be really a liquid. The explanation has since been shown to be that Lehmann's specimen of silver iodide was very impure, and that the pure substance even in the cubic form is as hard, at any rate, as phosphorus is right up to within 2° of its melting point, 550°C . Lehmann thought, however, and published his view, that he had discovered a “liquid crystal.”

Late in the year 1888 the attention of Prof. Lehmann was called by Dr. Reinitzer of Prague to another similar case to the supposed one of silver iodide, that of cholesteryl benzoate, $\text{C}_6\text{H}_5 \cdot \text{COO} \cdot \text{C}_{27}\text{H}_{45}$, which, according to

his observation, appeared to have two melting points, and between the two to exhibit what seemed to be double refraction. For after melting at 145° it changes, with continued heating, to a turbid liquid possessing the doubly refractive property, and appears to consist of an aggregate of minute crystals flowing as readily as oil, until at 178° it suddenly becomes a clear isotropic liquid. In 1890, within little more than a year, Dr. L. Gattermann discovered two more substances, para-azoxy-anisol (I) and para-azoxy-phenetol (II), which Lehmann further inves-

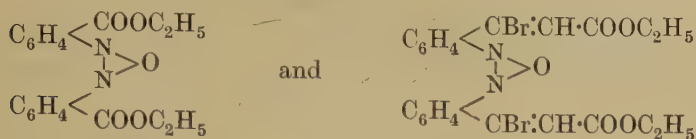


tigated, and found to be also cases of "liquid crystals," the former between 116° and 134° , and the latter between 134° and 165° . They form a turbid melt on fusion, composed of spherical drops with a dark kernel, and showing dichroism in polarised light; also two different colours in different directions, often as yellow and white alternate sectors, and a black cross under crossed Nicols.

In the case of para-azoxy-phenetol, for instance, when the crystals are warmed on a microscope slide, they become suddenly converted, at 134° C., into a substance which retains the shape of the crystal, is strongly doubly refractive, and becomes four times dark when rotated on the stage between crossed Nicols, like a true crystal. Yet all the time it is liquid and at once distorted if touched, but returns more or less to its former shape on removal of the disturbance. If heated further to 165° , it passes into a third form, a true liquid, which can be made by the addition of a little colophony resin to contain spherical drops of the birefringent liquid.

Further substances of similar character were later described by Vorländer, namely, the ethyl esters of para-

azoxy-benzoic acid and of para-azoxy-bromocinnamic acid. Their constitutional formulæ are :—



They were found by Lehmann to be the best cases yet observed, for they appeared to be uniaxial rectilinear prisms, with slightly rounded edges but with nearly sharply

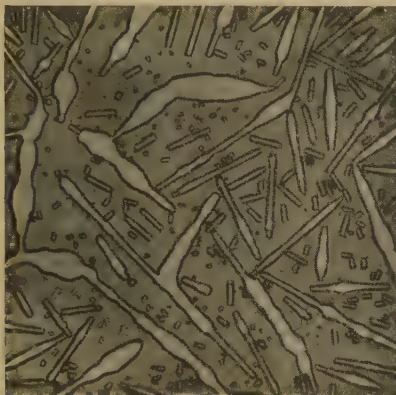


FIG. 70.—Ethyl Ester of Para-azoxy-bromocinnamic Acid.

defined basal plane or pyramidal end-faces, which were colourless in the direction of the axis, but yellow in other directions. They are shown in Fig. 70. When two individuals approach each other they first set themselves parallel with a jerk, and then coalesce, flowing into each other to form a single large “liquid crystal.”

But the most remarkable case of all is undoubtedly that of ammonium oleate, $\text{C}_{18}\text{H}_{33}(\text{NH}_4)\text{O}_2$, which shows the “liquid crystal” form at temperatures only very slightly above the ordinary. Lehmann found that when this salt of oleic acid is attempted to be crystallised from alcohol, by simply allowing a warm solution in alcohol to cool,

large "crystals" are obtained, which are nearly invisible in ordinary light, owing to their refractive index and that of the mother-liquor being very nearly identical. But in polarised light under crossed Nicols they are clearly revealed, being doubly refracting and polarising brightly, as steep double pyramids with more or less rounded edges, and showing uniaxial optical properties. A field of them under the microscope is shown in Fig. 71. That they are

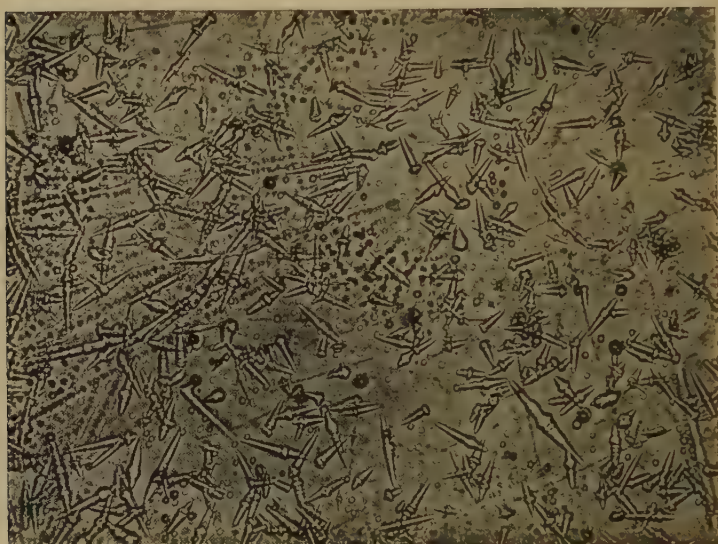


FIG. 71.—"Liquid Crystals" of Ammonium Oleate.

liquid is shown by touching the cover-glass, when they become distorted by the slight compression, but immediately recover their shape on removal of the pressure. Moreover, if one of them be broken into two parts, each part grows again into a perfect double pyramid with great rapidity.

The two refractive indices, corresponding to the ordinary and extraordinary rays, of several of these substances, have actually been determined by two independent investigators, Dorn and Stumpf. The "liquid crystals" also

appear to be influenced by a magnetic field, for both Lehmann and E. Bose have independently observed that when the magnet is excited the molecules or groups of molecules forming the "liquid crystal" structural unit set themselves parallel to each other with respect to their axes, and the liquid clears, the turbidity disappearing. Bose concluded that the molecules are ellipsoidal, while Lehmann considered the evidence to indicate a lamellar shape. In any case they set themselves in a definite position between the micro-slip and the cover-glass, the long axis of the Bose ellipsoid, or the Lehmann plate-surface, being set up perpendicularly to the glass surfaces, under the influence of the magnet.

There is one feature, as regards chemical constitution, common to all the substances which form "liquid crystals," as was first pointed out by Vorländer, and which probably affords the key to the explanation of the phenomenon. It is, that they are all elongated molecules. The principal aliphatic compound, ammonium oleate, is notoriously a long-chain compound, oleic acid, $C_{18}H_{34}O_2$, being one of the series of unsaturated organic acids having the general formula $C_nH_{2n-2}O_2$. The most of the aromatic compounds which form "liquid crystals" are para-derivatives of benzene, C_6H_6 , the two side-chains replacing the hydrogens in the benzene hexagonal ring at opposite ends of a diameter, being attached like wings, so that the compound is elongated on each side of the ring. Even by the constitutional formulæ, which have been given on pp. 220, 221 with the object of showing the fact, great extension of the molecules is indicated. Vorländer has also shown that the presence of doubly linked carbon and nitrogen atoms is particularly favourable for the production of "liquid crystals." For instance, the substance anisaldazine, $CH_3O \cdot C_6H_4 \cdot CH : N : N : CH \cdot C_6H_4 \cdot OCH_3$, is obviously a long-chain compound and also contains both doubly linked carbon and doubly linked nitrogen atoms.

Leaving out of consideration the fatty organic-acid salt ammonium oleate, in which it is only a question of crystallisation from alcohol, the substances behaving as "liquid crystals" are usually solids at the ordinary temperature, which melt on the stage of the crystallisation-microscope under the heat of the miniature Bunsen lamp, which is fitted under the stage of that microscope as made by Zeiss. On allowing the melt to cool, accelerated if necessary by use of the little air blasts also supplied for the purpose, the "liquid crystals" form at some specific temperature, and can be studied as long as the temperature can be adequately regulated. On cooling further, the ordinary solid form of the substance crystallises out, usually in branching, radiating, or wheel-shaped forms. One of the most beautiful experiments with these substances is that with cholesteryl acetate, $\text{CH}_3 \cdot \text{COO} \cdot \text{C}_{27}\text{H}_{45}$, which proceeds exactly as stated, ending with the formation of beautiful crucifera-like flowers of the solid form, the intervening space between which eventually gets filled up with long radiating needles, both flowers and needles polarising brilliantly under crossed Nicols, the flowers exhibiting a black cross.

The best explanation yet advanced as to the nature of "liquid crystals" is due to Bose, and is known as the "Swarm Theory," which he propounded in 1907. It is practically based on the fact already commented upon, that the molecules are always very extended ones. If two such elongated molecules approach each other within half their length, their free rotation is prevented in all directions except that of their length, so that a more or less parallel position is necessarily assumed. A bundle or "swarm" of such molecules arranged parallelwise will have the symmetry of a rotation figure, and behave somewhat like a uniaxial crystal. Now no biaxial interference figure in convergent polarised light has ever been observed with "liquid crystals." This is the more significant as

the vast proportion of organic compounds crystallise in the three biaxial systems, and more than fifty substances are now known exhibiting the phenomena of "liquid crystals." Each individual swarm will be clear and transparent, but between the swarms light will be scattered and the observed turbidity thereby caused. The molecules in a single swarm, when confined in the thin film between the micro-slip and the cover-glass, will all be arranged end on, all parallel to themselves and perpendicular to the glass plates. They will take up this attitude very readily, owing to molecular cohesion, and it is in this position that they afford the uniaxial interference figure in convergent polarised light, as illustrated diagrammatically in Fig. 72

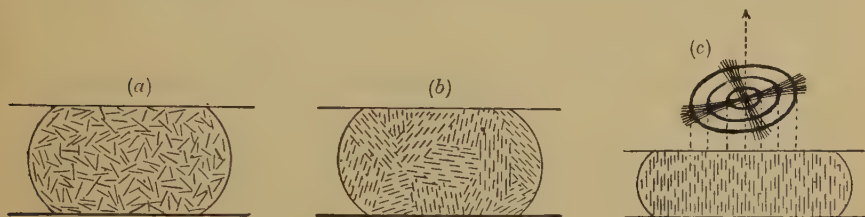


FIG. 72.—Bose's Swarms.

at (c). At (b) in the figure a number of different swarms, each with parallel molecules, are seen forming in the cooling liquid; while at (a) is shown the promiscuous arrangement of the molecules in the original true liquid. The fact that Vorländer's later preparations of complex aromatic compounds exhibit optical activity is readily explained by the fact that the molecules themselves are enantiomorphous.

After the introduction of X-ray crystal analysis it became very obvious that it was desirable to invoke its aid in elucidating the mystery of "liquid crystals," and of testing Bose's views by ascertaining the structure, if any, of these remarkable substances. Such an investigation was carried out in the laboratory of Prof. von Laue himself by J. S. van der Lingen, using as the substances experimented with para-azoxy-anisol, para-azoxy-phenetol,

anisaldazine, and amyl cyanobenzylidene-aminocinnamate. The result was conclusively negative as regards crystal structure, no trace of space-lattice structure having been indicated. Parallelwise-arranged molecules, or similarly orientated ellipsoidal molecules with one axis only fixed in space, would account for all the X-ray results, and for all the phenomena of "liquid crystals."

In this connection too it is interesting to remember that Müller and Shearer, in their recent work (see pp. 168, 169 in Chapter VIII) in Sir William Bragg's laboratory on the X-ray analysis of the long-chain fatty acids, found that those elongated molecules also arranged themselves perpendicularly to the layer, which had been formed by pressing the substance on to a glass plate as the most convenient support while subjecting them to the X-rays.

It would thus appear that "Liquid Crystals" are not really crystals at all, but a highly interesting intermediate form of matter, in which the molecules are no longer free to roll about as in a liquid, and yet are not arranged in a crystal structure but merely in bundles, parallelwise, owing to their length or extended nature and shape, and partly aided in many cases, doubtless, by their viscosity. The unusual play of molecular forces between such large and extended molecules would, of course, also be a powerful factor in producing swarms. The long controversy, which raged between Vorländer, who stood out even more strongly than the late Prof. Lehmann himself (who, unfortunately, died last year, 1924), for a space-lattice crystal structure, and Tammann, who utterly negatived the idea of anything but an ordinary emulsion, is thus apparently happily settled, the truth lying, as so often happens, between the two extremes.

CHAPTER XIII

FEDOROV'S CRYSTALLOCHEMICAL ANALYSIS

FROM time to time the great fundamental questions inevitably arise, "Why does a particular substance crystallise in a specific characteristic form?"—"What determines the choice of its form?"—"Shall we ever be able to predict from its chemical constitution what the crystalline form of a given substance will be?", and "Are we ever likely to be able to recognise a substance, however obscure or rare, merely by inspection or brief laboratory examination of its crystalline form?"

As regards the first two questions great strides have been made towards answering them, by the recent remarkable development of the analysis and elucidation of crystal structure by X-rays, and its confirmation of the main laws already established by crystallographers, and by the definite description of every one of the 230 "space-groups" corresponding to the only possible modes of arrangement of chemical atoms (regarded first as points, then as real entities) in crystals. As regards prediction, that has already been achieved for certain missing members of isomorphous series, just as the properties of the few missing chemical elements, for which spaces still remain in the periodic table, have been predicted. But as regards the prediction of the crystal properties of unconnected substances, that yet remains to be attempted.

There have recently been published, however, two monumental works, the first being the "Chemische Krystallographie" of Prof. P. von Groth, in which all the crystallographic data published up to the time of com-

pilation, concerning several thousand solid substances, is recorded in brief and concise form, employing the ordinary and generally accepted nomenclature of crystallography, on the principles given forth by Miller in Cambridge in 1839. This work is becoming more of a "stand by" every year, and is of the utmost value to all workers with crystals. It is a great satisfaction that the veteran founder and editor for fifty years of the *Zeitschrift für Krystallographie* and Emeritus Professor of Mineralogy at Munich should have been able to complete this great work.

The second is "The Crystal Kingdom," by the late Prof. E. S. Fedorov of Petrograd (St. Petersburg). This posthumous work is really a great table, embodying crystallographic data for 7,400 substances, which Fedorov considered to have been adequately described and measured goniometrically. The information is compressed into the compact form of a symbol, his "Complex Symbol," which occupies less than a square inch of space. The idea is, that by an investigation of about an hour's duration or less, sufficient knowledge can be gained of any crystallised substance in question, to enable that symbol in the table to be found which corresponds to the substance, and thus to identify the latter. The method has been tested by a few enthusiastic disciples of Fedorov, who studied with him in Russia before the war and revolution, and in their hands has proved remarkably successful. For instance, Mr. T. V. Barker of Oxford, one of those referred to, records in an article in *The Lancet* for May 26th, 1917, how he received from a correspondent a packet containing a crystal of unknown composition, and of less than a quarter of a gramme in weight, with the query, "What is it?" After an examination lasting 65 minutes it was decided that the substance was salol (phenyl salicylate), without injuring the specimen.

Unfortunately, besides basing his method on a form of the geometrical theory of crystal structure which is peculiar

to himself, Fedorov, like Prof. Victor Goldschmidt of Heidelberg, used the two-circle goniometer, and his method requires all measurements to be made with this instrument in azimuths and polar distances, instead of the more general and usual Wollastonian and Millerian mode of measuring the interfacial angles directly in their zones with a first-class single-circle goniometer. The theodolitic method may be of special value as regards rapidity of work, as one setting of the crystal may suffice, a desideratum for the mere purpose of identification. But the important zonal relationships are not so well brought out, nor even are whole zones often completely measured, and pitfalls in the use of the method and the interpretation of the results are numerous, as the literature abundantly proves. Also the crystal elements are not so readily and directly calculated. Moreover, nothing is accomplished which, given perhaps a somewhat longer time, which must never be spared if research work is to be of value, cannot be better done with the single-circle goniometer constructed by a first-class optician, on the dividing of the one circle of which special pains can be taken to get the utmost accuracy. Also, which is particularly important, crystallographic data of the ordinary, and not the two-circle kind, are required by the X-ray crystal analysts, who are now turning out such a volume of results. So for all these reasons the two-circle method cannot be recommended for all the ordinary crystallographic purposes of research to-day, and it is scarcely to be supposed that Fedorov's method, nor his remarkable table, a monument of industry, are likely to come into general use. If the table can somehow be brought into line with the usual methods, and freed from his peculiar form of crystal-structure theory, it may in the end lead to the great usefulness of a reconstructed table.

Incidentally it may be mentioned that Prof. Miller, who in Cambridge gave to crystallography its current and unsurpassable method of labelling crystal faces, and of

identifying, localising, and describing them, himself constructed a two-circle goniometer, which is preserved in the Mineralogical laboratory of the University. He appears not to have made much use of it, however, finding the single-circle instrument all that was needed and more convenient with his own inimitable methods.

It may be of interest, however, to give a brief outline of the Fedorov method. The results of the azimuth and polar distance two-circle measurements are plotted on a stereographic net, and the crystal system deduced from zonal angles graphically determined (not having been directly measured), with the aid of a three-point compass and the stereographic net. The crystal facial indices are determined graphically with the aid of the gnomonic projection, and the axial ratios by the Goldschmidt method based on the gnomonic projection, preferably confirmed by the usual method of the solution of spherical triangles. The "correct setting" of the crystal is then worked out, from the principles that the proper primary faces (100), (010), and (001), with also (111), are those of maximum reticular density as regards the nodes or points of the space-lattice, and that such should be chosen, if two or more alternatives are open, by the indications of cleavage (densest planes in points), relative development of faces, and other purely crystallographic considerations. When the setting is thus correctly diagnosed, the complex symbol is drawn up.

The Fedorov "Complex Symbol," as stated by T. V. Barker and Miss M. A. Porter,* is an expression which indicates simultaneously both the type of structural arrangement and the characteristic angles of the crystal, if necessary, after a suitable homogeneous deformation or shear. The initial term of the symbol is the number 6, 4, or 3, according as the crystal is held to approximate most closely to a hexagonal-, tetragonal-, or trigonal-rhombohedral form respectively. When necessary, this number is

* *Journ. Chem. Soc., Trans.* 1920, **117**, 1311.

followed immediately by a letter. *h*, *c*, or *d*, respectively indicating, in Fedorov's peculiar phraseology, that the arrangement is "hexahedral," that is, that of a simple space-lattice, "octahedral," that of a centred lattice, or "dodecahedral," that of a face-centred lattice. Thus $4h$ signifies that the type of the structural arrangement is that of a simple tetragonal space-lattice, whilst $3d$ indicates the face-centred trigonal-rhombohedral lattice as being the structural type. All remaining terms of the complex symbol are numerical constants, representing degrees of arc, which serve to characterise each crystal species. One of these, expressing in general the value of the angle (after a shear) between the correct basal plane and primary pyramid, is especially important in Fedorov's classification, so by way of contrast he encloses in brackets all other terms necessary to express the angular deviations of the lattice from an ideal hexagonal, tetragonal, or trigonal form.

Thus in the symbol " $(6) 37\frac{1}{2} (+ 3)$," the first term signifies that the crystal approaches ideal hexagonal symmetry, the second term that the principal angle is $37\frac{1}{2}^\circ$, and the third term that the prism angle has the value $60^\circ + 3^\circ$, that is 63° , instead of the 60° proper to an ideal hexagonal lattice. The absence of any further term indicates that the system is orthorhombic. On the other hand, in the symbol " $(3h; + 2) 58 (0)$ " we have a new kind of numerical term, namely, $+ 2$, immediately following the structural term $3h$. This means that the angle between two of the structural planes is not 90° but $90^\circ + 2^\circ$, in other words, that the crystal is monoclinic with an axial angle $\beta = 92^\circ$. The last term, (0) , refers, as before, to the prism angle, and means that the deviation from the ideal value of 60° is nearer 0° than $\frac{1}{2}^\circ$. The angles in the complex symbols are only given to the nearest half degree, since this is the limit of accuracy of the graphical methods employed. In the tables all crystals belonging to the same type, say $4h$ or $3d$, and so on, are collected together, and

then mutually arranged in order according to the value of the principal angle. Any well-developed crystalline substance which has once been measured, and placed in the dictionary in the place required by its complex-symbol, can be identified on any future occasion; for it is only necessary to measure the crystal to be identified, in the cursory abbreviated manner indicated, to deduce its complex-symbol from the development on the stereographic net, and to refer to the dictionary table for the symbol in question, when the composition of the substance will be found stated opposite to the symbol.

The latter part of the statement would appear to assume that the determination of the complex-symbol is a very easy matter; but it would require an observer to be steeped in Fedorov's methods, which means learning a new kind of crystallography based on a peculiar and very doubtful form of the theory of crystal structure. Moreover, the whole method and investigation only contemplates an accuracy of half a degree, which to the author is naturally coarse and rough-and-ready in the extreme. It would exclude any discrimination between the members of isomorphous series. As regards this point, it may be of interest to record that when Fedorov's method was being tested, the author submitted a number of substances, and all but one were identified, that one being one of the double sulphates belonging to the hexahydrated monoclinic series described in Chapter V, and the identification was only carried in this case as far as to allocate the substance to this large series without being able to specify the particular member.

Fedorov is entitled to the greatest possible credit for the ingenuity of this method of crystallochemical analysis, and it is only too great a pity that it should be handicapped by the drawbacks which have been enumerated. One part of it, however, the diagnosis of the correct setting, as to which way up and with what primary faces the crystal

shall be arranged for descriptive purposes, is at any rate of great permanent value. It may be mentioned, for instance, that a recent X-ray analysis of the substance iodo-succinimide by Miss K. Yardley, carried out in the laboratory of Sir William Bragg, indicated that the currently accepted mode of "setting" the crystal did not correspond to the structure as determined by X-rays. The remeasurement of the substance was undertaken by the author at Miss Yardley's request, and also the optical properties and density were determined, and it was found that the setting required by the X-ray results corresponded to the correct setting as determined on the Fedorov principle. In this method of his we certainly have a very good way of diagnosing the correct setting. Also, of course, the work of Fedorov, even although it be founded on his peculiar views of crystal structure (which will be found fully described in Chapter XXXIV of Vol. I of the author's "Crystallography and Practical Crystal Measurement," 1922 edition), as dependent on the types of polyhedra capable of filling space without interstices, in independently describing, and indeed discovering (for he was first, but published in Russian) the 230 space-groups which form the prototypes of all crystal structure, at the same time as, or even a little earlier than, Schoenflies in Germany and Barlow in England, will ensure for him the credit due to so fundamental an advance.

CHAPTER XIV

GENERAL CONCLUSIONS

IN concluding this account of the present position of Chemical Crystallography two facts, derived from the most recent work and confirmed by all that has gone before, stand out conspicuously. They are first, that :

The Chemical Molecules and the Structure of the Crystals which they build up in the solid state of their aggregation are interdependent, as regards respectively their stereometry and symmetry. For any symmetry which the molecule possesses, by virtue of the stereometric arrangement of its atoms, is carried over into the crystal ; and the symmetry of the crystal either reflects immediately that of the molecule, or, much more frequently, is of a higher class, produced by the symmetric physical combination of two or more (rarely reaching eight) molecules to form the unit-cell of the space-lattice structure. The greater the symmetry of the molecules (as regards the stereometric arrangement of their atoms) the fewer will be required to make up the most stable space-lattice unit ; on the other hand, more will be required when the molecule is entirely without symmetry, asymmetric. The stereometric arrangement of the atoms in the molecule thereby takes on a new significance, little suspected by Wislicenus when he spent his great energies in elaborating the science of chemical stereometry. The study of the crystals of a substance, therefore, is in the future bound to throw more light on chemical constitution and the nature of the chemical molecules, and indeed should be a new mode of attack available for the solution of all cases of ambiguity

or special difficulty as regards the arrangement of the atoms within the molecule. The first outstanding fact thus connects the Crystal with the Molecule.

The second fact connects the Crystal with the Atom, and is, that: The difference in Atomic Structure, on passing from one chemical element to another, is clearly reflected in the Structure of the Crystal built up by the Atoms concerned. This is most clearly seen in the small but definite and very regular progression of the crystal structure and physical properties which occurs in a eutropically isomorphous series, such, for instance, as those in which the alkali metals potassium, rubidium, and caesium are the interchangeable metals. The fact that the atoms of rubidium are larger and more complex than those of potassium, by the addition of eighteen electrons, one or two (according to the two versions of Langmuir or Bohr) whole shells, and that again those of caesium are similarly larger and more complex by the same number eighteen of electrons, is perfectly interpreted in the structure and physical properties of the crystals containing respectively each of these alkali metals in turn as the dominant base, and especially and strikingly by the regular increase in the size of the unit cells of the space-lattice, accompanied as it is by the beautifully regular alteration of the crystal interfacial angles and the whole of the physical constants and characters.

The results of crystallographic investigation being thus in full agreement with the contemporaneous progress in our knowledge of the structure of the atom, we may fairly enquire how far future research on crystals may be expected to assist in clearing up the details of atomic structure, and replacing the present conflicting views or versions of the theory by the truth, which must lie somewhere between them. There can be no longer any hesitation in accepting the principle that chemical action has to do with the outer electrons of the atom-system. The remarkable case

of the rare earths, which owe their extraordinary similarity to the fact that the addition of electrons to evolve them one after the other occurs in the interior of the atom-system and not, as usual, to the outer shell, would alone prove this. It can therefore be accepted with confidence and almost as unreservedly that the stereometric arrangement of the atoms in the molecule is the result of the mutual interaction of the outer electrons of the various atoms on each other, and of the electrostatic attractions and repulsions, or the sharing of electrons, resulting therefrom. Further, when the molecules thus produced take up the solid state they do so either by each molecule forming the unit-cell of the space-lattice, or by arranging themselves symmetrically in small groups of two, three, four, or so, to form the unit-cell, according to one of the schemes of structure possible to crystals, namely, that of one of the 230 space-groups or point-systems, which is the most stable form which that particular substance can take up by reason of the nature of its molecules. If the compound be a very simple one, such as rock salt, sodium chloride NaCl , the interaction of the outer electrons of the single atoms of the two elements sodium and chlorine, and the electrostatic forces thereby caused, would appear to be sufficient to hold the solid structure together, and it is unnecessary to seek for further forces between the molecules as such. The expression is often used that the structure in this simple case is one of "ions," but this is really the same thing otherwise expressed, and is not a happy term, as these atomic units of the crystal structure are quite different from the "ions" of dissociated dilute solutions. The key to the chemical action would indeed appear to be the striving after the formation of a stable outer shell of electrons, that is, to complete the shell as it is in the atom of the inert gas of the eighth group (neon, argon, krypton, or xenon); for example, the alkali haloids would appear to be formed by the metal—

say potassium—of atomic number 19, giving up one electron to chlorine, atomic number 17, thereby both atoms having 18 electrons, the atomic number of argon, which has the stable outer shell of eight electrons, the chemical combination occurring owing to the potassium atom and the chlorine atom thereby having respectively acquired a positive and a negative unit charge and consequently being electrostatically attracted to each other.

Moreover, even in fairly simple compounds, such as calcite, CaCO_3 , and sodium nitrate, NaNO_3 , the CO_3 group and the NO_3 group appear to act as entities, replacing the halogen element of a haloid salt, and so similarly that calcite and sodium nitrate are isostructural, whether isomorphous or not. Indeed we might adopt Werner's co-ordination idea, and write them $\text{Ca}[\text{CO}_3]$ and $\text{Na}[\text{NO}_3]$.

But in the cases of more complicated molecules, such, for instance, as those of naphthalene, where more than one (in this case two) molecules go to form the unit cell, it is certain that each molecule is fixed by the attachment of certain very definite points on its own structure to other equally specific points on the structure of another molecule, the precision of the adjustment being very exact, indicating very definite form on the part of the molecule, and that the forces exerted have very short ranges. In the case of naphthalene the molecules arrange themselves alongside each other so that the α -hydrogens of each molecule attach themselves to the carbon atoms of the neighbouring molecules, while the β -hydrogen atoms attach themselves to the β -hydrogen atoms of neighbouring molecules, thus locking the structure together, molecule to molecule, to form the space-lattice cells, and the cells to each other, so that the whole edifice is as stable as the most perfect engineering structure.

Moreover, Sir William Bragg appears to have proved definitely that the carbon atom has a tetrahedral arrangement of electrons in its outer shell, and has actually located

singularities of structure at the tetrahedral positions, and something of the nature of connecting electrons at these positions. The latest experiments with diamond and graphite have brought these facts out prominently. The forces holding the carbon atoms of the diamond together have been proved to be primarily exerted along four lines drawn from the centre of a tetrahedron to its corners, and there is a strong resistance to change in those directions. There are thus four electronic orbits all alike in the carbon atom as it exists in the diamond. And all this tallies with the fact that carbon belongs to Group IV of the periodic classification, with atomic number 6, and is thereby a tetrad with four electrons more than helium, atomic number 2, the first of the inert gases and the two electrons of which form the innermost and only shell of that atom; the four electrons may therefore be supposed to be on the outer shell, to complete which the number contained by neon (atomic number 10) would have to be attained, namely, four more. The agreement between chemical facts and crystal structure is very obvious in all these observations, and when one adds to them the correspondence which has been proved between the diamond form of the carbon atom and the carbon of the aliphatic series of organic compounds, the concensus is really very striking.

In the case of the carbon of graphite, the electrons of the outer shell are, of course, four as before for diamond carbon, but three only of them have like orbits, while the fourth has been definitely shown to be different; this latter odd electron will travel relatively further, and be more loosely attached to the nucleus, thus explaining the colour, opacity, and conductivity of graphite. Indeed, it has been shown that the structure of the carbon atom of graphite, and the forces radiating from it, agree with the hexagonal ring structure of the aromatic organic compounds as remarkably as do the properties of diamond carbon with the fatty series of carbon compounds. For

the latest research on graphite has afforded results which render it no longer in doubt that the graphite layer of carbon atoms is the diamond layer (both being in three-atom groups combining in pairs to form hexagons) pressed flat without any sideways extension, and with the distance between the layers much increased compared with the diamond layer-separation, rendering graphite one of the softest and flakiest of substances, in striking contradistinction to the supreme hardness and rigidity of diamond.

Thus, in conclusion, we are fully justified, after a review of the extraordinary progress which has been made since Laue's discovery in 1912 of X-ray reflection by the planes of atoms in crystals, in the belief that the further study of pure crystallography, combining the results of X-ray analysis with those derived by the ordinary methods of crystallography, and especially expanded on the side of the physical properties (not only the optical), will enable still more far-reaching conclusions to be derived as to the ultimate structure of matter. It is certainly in this direction that we should look for the perfecting of the theory of atomic structure, to bring the conflicting views of the rival versions together, and thus to evolve the truth itself.

APPENDIX

LIST OF MEMOIRS COMMUNICATING THE RESULTS OF THE RESEARCHES DESCRIBED IN CHAPTERS III, IV, AND V

1. Connection between the atomic weight of contained metals and the magnitude of the angles of crystals of isomorphous salts. A study of the potassium, rubidium, and caesium salts of the monoclinic series of double sulphates $R_2M(SO_4)_2 \cdot 6H_2O$.—"Journ. Chem. Soc. Trans.," vol. 63, p. 337 (1893); and "Zeitschr. für Kryst.," vol. 21, p. 491 (1893).

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4. Comparison of the results of the investigations of the simple and double sulphates containing potassium, rubidium, and caesium, and general deductions therefrom concerning the influence of atomic weight on crystal characters.—"Journ. Chem. Soc. Trans.," vol. 69, p. 495 (1896); "Z. f. Kryst.," vol. 27, p. 252 (1897).

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7. The thermal deformation of the crystallised normal sulphates of potassium, rubidium, and caesium.—"Phil. Trans.," A, vol. 192, p. 455 (1899); "Z. f. Kryst.," vol. 31, p. 426 (1899).

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3. An instrument for cutting, grinding, and polishing section plates and prisms of mineral or other crystals accurately in the desired directions.—“Proc. Roy. Soc.,” A, vol. 57, p. 324 (1895); “Z. f. Kryst.,” vol. 25, p. 79 (1896).
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